UNITED STATES PATENT OFFICE.

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PROCESS OF SEPARATING NICKEL FROM COPPER IN ORE OR MATTE.

SPECIFICATION forming part of Letters Patent No. 579,111, dated March 16, 1897.

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To all whom it may concern:

Be it known that I, NOAK VICTOR HYBINETTE, a citizen of the United States, and a resident of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Processes of Separating Nickel from Copper in Ore or Matte, of which the following is a specification.

My invention relates to the separation of commercially pure sulfid of nickel from ores and mattes containing the mixed sulfids of nickel, copper, and, eventually, iron. This separation consists in smelting the mixture of sulfids now mentioned with certain chemical reagents, tending to produce certain changes in the molten mass, whereby sulfid of copper rises to the top and may be mechanically separated from the lower part of the bath in any convenient manner.

The only process heretofore known by which such separation is brought forth is to smelt the ore or matte with a salt of any of the alkaline metals, preferably niter-cake or salt-cake, under such conditions that the corresponding alkaline sulfid, preferably sulfid of soda, is formed in the bath. A mixture of metallic nickel and sulfid of nickel is thus separated from the molten mass. I have now discovered that the metal and compounds of manganese serve the same purpose and are preferable to the alkaline salts. If, therefore, the copper-nickel ore or matte is smelted with metallic manganese or any compound of manganese, or either of these together with a salt of any of the alkaline metals under such conditions that sulfid of manganese will exist in the molten bath, it will be found that sulfid of copper rises to the top with the sulfid of manganese.

The different chemical properties of the metals and their sulfids which cause this separation, and which it is necessary to know to understand the working of the process, are as follows:

First. The affinity for sulfur of manganese, copper, iron, and nickel is stronger in the order they now have been mentioned, so that the manganese has the greatest and nickel the least affinity for sulfur. When, therefore, manganese, copper, iron, and nickel are smelted together and sulfur introduced in small portions, manganese will be the first to combine with sulfur, then copper, iron, and, last, nickel.

Second. Commercial copper-nickel matte consists of sulfid of copper, sulfid of iron, sulfid of nickel, and metallic nickel. Of these, sulfid of copper is very readily soluble in sulfid of manganese, sulfid of iron is not so easily soluble, and sulfid of nickel and metallic nickel are practically insoluble in the same sulfid of manganese.

Third. Sulfid of nickel and metallic nickel dissolve sulfid of copper and sulfid of iron in almost any ratio.

Fourth. Pure sulfid of manganese is almost infusible, but melts readily if mixed with a small amount of sodium or potassium sulfid or a somewhat larger quantity of sulfid of copper or sulfid of iron.

Suppose now that the four metals, manganese, copper, iron, and nickel, are present in a molten bath together with a certain amount of sulfur sufficient to form saturated sulfids of all the manganese, copper, and iron present, but only a small proportion of sulfid of nickel, the rest of the nickel being left as metal, or, in other words, suppose that copper-nickel matte is mixed with sulfid of manganese. As sulfid of nickel and metallic nickel are practically insoluble in sulfid of manganese, a separation takes place. The top consists of sulfid of manganese, the bottom of sulfid of nickel and metallic nickel. As the sulfid of copper is more soluble in sulfid of manganese than in sulfid of nickel and metallic nickel, and as sulfid of iron is about equally soluble in both, it will be found that the top consists of all the sulfid of manganese, the larger part of the sulfid of copper, and about half of the sulfid of iron. The bottom consists of all the sulfid of nickel and metallic nickel, a small portion of sulfid of copper, and about half of the sulfid of iron.

It is evident that by removing the top and treating the bottom with new sulfid of manganese or metallic manganese or any combination of manganese and some matter containing sulfur, under such conditions as to form sulfid of manganese, the sulfid of nickel can be purified from sulfid of copper and sul-

fid of iron to an extent depending upon how many times the operation is repeated.

The experiment now described practically indicates the conditions I intend to bring about in my process. If, however, the amount of copper and iron to be separated from the nickel is small, it will be found advantageous to add a small proportion of any salt of the alkaline metals, preferably niter-cake or salt-cake, under such conditions as to form the corresponding sulfid, preferably sodium sulfid. This makes the top very fluid even if very little sulfid of copper or sulfid of iron is present. As already remarked, pure sulfid of manganese is almost infusible, but an addition of five per cent. sodium sulfid is enough to make it easily fusible.

The way I propose to carry out this process on a large scale is to smelt the combined sulfids with manganese ore (practically oxid of manganese) and a reducing agent, preferably coke, in any convenient furnace, preferably a cupola-furnace, and eventually add a small proportion of any salt of any of the alkaline metals, preferably niter-cake, to make the mass more fluid. The proportion of manganese added should be such as to give as a bottom part of the bath a mixture of nickel and sulfid of nickel with a small proportion of the copper, and as a top part a sulfid of copper and manganese practically free from nickel. The chemical reactions that take place during the smelting are the conversion of the manganese oxid into sulfid of manganese and the reduction of an adequate portion of the sulfid of nickel to metallic nickel, thus:

$$MnO_2+C=2CO+Mn;\ Mn+NiS=Ni+MnS.$$

The bottom should be treated over and over again in the same way as the original material until the percentage of copper is brought down to the desired point, and sulfur should be introduced, so as to keep most part of the nickel and all the copper as sulfid, as in the original matte. It is evident that when sulfid of manganese regenerated from the tops is used no addition of sulfur is necessary.

The top, containing principally the sulfids of manganese and copper, has to be treated for the production of copper and regeneration of manganese. This is effected in exactly the same way as ordinary copper matte is treated for production of copper. The top is calcined and smelted in a suitable furnace with or without addition of silica. If silica is used, the result is CuS and $MnSiO_3$, thus:

$$2SiO_2+CuO+MnO+CuS+MnS=2CuS+2MnSiO_3.$$

If no silica is used, the reaction is:

$$CuO+MnO+CuS+MnS+2C=2Cu+2MnS+2CO.$$

If this last reaction is carried out in a reverberatory furnace, it is therefore necessary to add any reducing agent, preferably coke. The regenerated sulfid of manganese can be used over again for treating new material, but when using silicate of manganese it will be found well to add some more basic oxid—for instance, lime—to force the manganese oxid out of its combination with silica, thus:

$$MnSiO_3+CaO=CaSiO_3+MnO,$$

the MnO acting as before explained about MnO_2.

The process works equally well whether metallic manganese, or an alloy of manganese, or an oxid of manganese, or a sulfid of manganese is employed. If the material to be treated is very rich in sulfur, metallic manganese or oxid can be used, but if the material to be treated is poor in sulfur then sulfid of manganese must be employed, either added as such or produced in the process by the addition of sulfur in some form to the manganese charged in the furnace.

I claim—

1. The process of separating copper from nickel in their sulfur compounds, consisting in fusing the mixed sulfids, treating the fused mass with sulfid of manganese and thereby effecting solution of the copper sulfid in said manganese sulfid, allowing the nickel to subside and removing the supernatant sulfids of manganese and copper.

2. The process of separating copper from nickel in their sulfur compounds, consisting in fusing the mixed sulfids, treating the fused mass with sulfid of manganese and an alkali sulfid and thereby effecting solution of the copper sulfid in said manganese sulfid, allowing the nickel sulfid to subside and removing the supernatant sulfid of manganese and copper.

3. The process of separating copper from nickel in their sulfur compounds consisting in fusing the mixed sulfids, treating the fused mass with sulfids of manganese produced by mixing the raw materials therefor with the ore or matte and thereby effecting solution of the copper sulfid in said manganese sulfid, allowing the nickel sulfid to subside and removing the supernatant sulfid of manganese and copper.

4. The process of separating copper from nickel in their sulfur compounds consisting in fusing the mixed sulfids, treating the fused mass with sulfid of manganese and sulfid of an alkali produced by mixing the raw materials therefor with the ore or matte and thereby effecting solution of the copper sulfid in said manganese sulfid, allowing the nickel sulfid to subside and removing the supernatant sulfid of manganese and copper.

Signed at New York city, in the county and State of New York, this 11th day of January, A. D. 1896.

NOAK VICTOR HYBINETTE.

Witnesses:

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