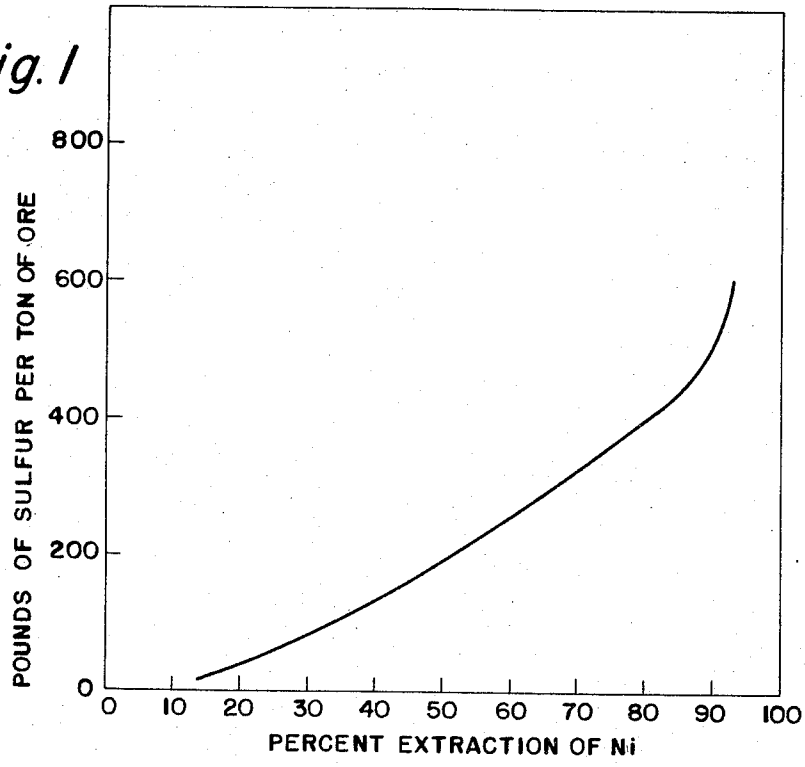
Jan. 23, 1968 E. F. FITZHUGH, JR., ET AL 3,365,341
NICKEL RECOVERY PROCESS
Filed July 21, 1965

Fig. 1



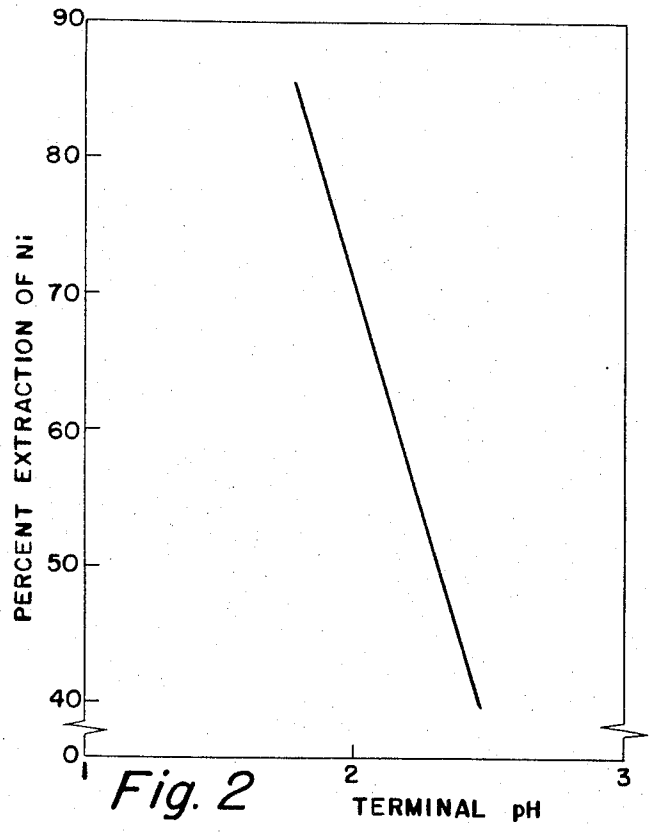


Fig. 2

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NICKEL RECOVERY PROCESS

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Continuation-in-part of application Ser. No. 388,042, Aug. 7, 1964. This application July 21, 1965, Ser. No. 473,575

15 Claims. (Cl. 75—119)

ABSTRACT OF THE DISCLOSURE

This invention comprises a process for extracting nickel from a nickel-bearing ore of the silicate or oxide type in which a water slurry of finely divided sulfur and finely divided ore, in a proportion of 150–800 pounds of sulfur per ton of ore, is heated under pressure at a temperature in the range of 100–300° C. and a pressure of at least 100 pounds per square inch, until essentially all of the sulfur has been reacted. The nickel is thereby converted to nickel sulfide which can be processed for recovery of the nickel by various techniques, advantageously by oxidation and preferably at a temperature of about 100–300° C.

This invention relates to a process for the recovery of nickel from ores. More particularly, it relates to a process for the recovery of nickel from ores containing nickel in silicate or oxidized form. Still more particularly, the invention relates to a process in which the nickel is converted to a more easily recoverable form by the reaction of sulfur with the nickel component of said ore. Cobalt is likewise converted to a comparable and more easily recoverable form.

This application is a continuation-in-part of copending application Ser. No. 388,042, now abandoned, filed Aug. 7, 1964.

There are various references in the literature to processes attempting to extract or recover nickel from various types of ores. Such recoveries are complicated by the fact that the reagents used also react with the magnesium and iron compounds that are also generally present. Most of these suggested processes are impractical for the reason that there is no selectivity between the sulfur reaction with the nickel component and with the magnesium and iron components. Therefore considerable amounts of reagent are required to convert the nickel to a recoverable form because of the amounts simultaneously reacted with the iron and magnesium. The excessive amounts of such reagents therefore required have made the processes relatively expensive and thereby commercially unattractive.

Pyrometallurgical processes have been attempted for the direct reduction of the nickel from its oxidized state, e.g., silicate or oxide, to the metallic state or other reduced state suitable for leaching. For example Hills' Patent 3,100,700 discloses a process for reducing nickel from ore by the high temperature, preferably 1200–1500° F., treatment with hydrocarbon oils. Such pyrometallurgical processes all require a preliminary drying step. Since most silicate and oxidized ores contain 15 percent or more moisture, a significant expenditure for fuel is required to drive off this moisture.

Furthermore, this Hills' patent has been investigated and found that the reported high efficiencies are obtained with extreme leaching. Thus, as shown in the various examples the standard or normal ammoniacal leaching step is repeated three times. This, as well as the predrying and high temperatures, involves considerable expense.

There are various leaching processes used to remove the nickel from ore using sulfuric acid, sodium sulfide,

etc. For example, Rodrian Patent 1,728,735 describes a process in which the ore is treated with sodium sulfide solution either preformed or formed in situ from caustic soda and sulfur. However, the large amounts of caustic required make this process economically unattractive. Likewise, because sulfuric acid also reacts with the magnesium and iron compounds present, the excessive amounts of acid required makes sulfuric acid leaching too expensive for commercial use.

Consequently prior processes have the disadvantage of expensive operation either in the necessity to dry the ore in the pyrometallurgical processes or in the amount and/or type of leaching reagent used in the wet processes.

The present process has the advantages of avoiding the expensive ore-drying step and of using a very inexpensive reagent, namely elemental sulfur, to recover the nickel from its ores by a very efficient and relatively simple process.

In accordance with the present invention, it has been found that the nickel can be converted to a recoverable form by reaction of the nickel component of the ore directly and much more economically with elemental sulfur in the presence of water to form nickel sulfide, which can be recovered as such and the nickel value recovered therefrom or which can be oxidized to a soluble form and the nickel value thereafter recovered according to various procedures. While the sulfur also reacts with the magnesium and iron, the reaction is with a much less expensive reagent than the sulfiuric acid, caustic and other leaching agents and this process is therefore much more commercially attractive. Moreover since this is a wet process, the necessity and expense of drying the ore is avoided. Furthermore, since the sulfidization reaction requires a much lower heat input and the oxidation is exothermic, the heating expense is much less than in the pyrometallurgical processes as exemplified by Hills.

Various aspects of the invention are illustrated by the drawings.

FIG. 1 is a plotted curve showing that, for a substantial portion of the curve, the efficiency of removal of nickel from the ore is substantially a straight line function of and increases with the amount of sulfur used.

FIG. 2 is a plotted curve, substantially a straight line function, illustrating that for a certain amount of sulfur and with other conditions standardized, the pH of the aqueous solution at the termination of oxidation indicates the degree of nickel extraction.

The process of this invention is very appropriate for use with ore containing approximately 1–6% nickel. As indicated, the ore can also contain substantial amounts of iron, magnesium and cobalt, for example. Moreover, the process of this invention is similarly useful in the recovery of cobalt. The cobalt and nickel can be separated from each by known processes, such as electrolytic deposition, etc.

In effecting the sulfidization by the process of this invention the ore is first finely divided and mixed with sulfur to form a water slurry. The ore is ground to a very fine particle size, advantageously fine enough to pass through a 100 mesh screen, preferably through a 200 mesh screen (Tyler). The grinding operation can be effected in a ball mill or other appropriate comminuting device, either before or simultaneously with the mixing of sulfur.

In preparing the slurry for the sulfidization operation, the upper limit on the amount of water is determined by practical limits such as volume of equipment per ton of ore throughput. The minimum amount of water is that which will give the slurry an appropriate flow characteristic. A solids content of about 35% has been found very satisfactory. As high as 40% solids can be used although

with some ores this is quite viscous. Eventually the slurry is diluted to about 30% solids for ease of stirring.

The resultant slurry is placed in a pressure vessel and heated to 100–300° C., preferably 215–245° C., for an appropriate period. For reaction at 235° C., particularly effective results are obtained with a heating period of 2–4 hours. With lower temperatures longer heating periods are advantageous, although generally no more than 12 hours is necessary, and with higher temperatures, shorter reaction periods are permissible. For example, a reaction temperature of 300° C. gives satisfactory results within 15–30 minutes.

In the practice of this invention, approximately 150–800 pounds of sulfur is used per ton of ore, preferably 325–450 pounds per ton. This depends somewhat on the amount of nickel in the ore and also on the amounts of iron and magnesium present. As much as 20 pounds of sulfur per pound of nickel can be used, again depending on the amounts of iron and magnesium present. As shown in FIG. 1, the efficiency of the nickel extraction increases within the indicated range as the proportion of sulfur is increased.

In a typical operation with an ore containing 2.3% nickel, 400 pounds of sulfur per ton of ore is advantageously used at a temperature of approximately 235° C. for 2–4 hours.

During the sulfidization a pressure of at least 100 p.s.i. is maintained. The upper limit on the pressure is determined only by practical considerations so that generally it is not desirable to exceed about 1200 p.s.i.

One of the advantages for the process of this invention is the fact that the relatively inexpensive 316 stainless steel can be used in the sulfidization and oxidation equipment without corrosion. Various other nickel recovery processes require exotic materials of construction such as titanium, etc.

At the beginning of the sulfidization the slurry is practically neutral, having a pH of about 7–7.5. At the end of the sulfidization the solution has a pH of approximately 6. At this point there is no nickel in solution but there is approximately 20–28% of the magnesium content of the ore dissolved in the water. This probably results from the reaction of a limited amount of sulfuric acid which is believed to be formed during sulfidization.

The sulfidized nickel can be recovered in accordance with several of the various methods for separating nickel sulfide from ores. A novel and preferred process for recovering the sulfidized nickel is to oxidize the nickel sulfide to nickel sulfate solution. While oxidations in the presence of ammonia are described in the literature, applicants prefer to oxidize in the absence of ammonia, as described herein. This avoids the need for special provisions to recover or keep the ammonia in the equipment, avoids precipitation of nickel, probably with iron, and in general gives improved results.

Prior to the oxidation step the slurry from the sulfidization is usually diluted to about 20% solids although 25–30% slurries may be used depending on the viscosity of the specific slurry.

In the oxidization step, the sulfidized ore slurry is advantageously cooled to the temperature desired for initial oxidation and then oxidized with an oxygen-containing gas, such as air, air-oxygen mixtures, concentrated oxygen, e.g., 21–100% oxygen, oxygen-supplying chemicals, etc. This oxidation is conducted until essentially all sulfides have been oxidized.

The conditions for oxidation will vary according to the type of oxidizing agent used and the type of ore. For example, with a particular ore, oxidation with substantially pure oxygen can be effected at 100° C. for six hours at 40 p.s.i.g. With air being passed through the slurry at 160 p.s.i.g., the oxidation is completed in 6 hours at 100° C. With air at 140 p.s.i.g., the oxidation is completed at 5.7 hours at 120° C. With air at 400 p.s.i.g., the oxidation is completed in 2 hours at 200° C. The reaction can be started at room temperature, and because of the exothermic character of the reaction the temperature rises, and the desired temperature is maintained by removing excess heat. Generally, however, it is desirable to start with an appropriate temperature to give an adequate initial oxidation rate such as 70° C. or higher. In certain cases it is actually desirable to cool the reaction mass from a prior reaction step to the reaction temperature desired for this oxidation.

With small reactors such as laboratory equipment, the heat losses make it desirable to supply external heat to maintain a temperature of at least about 70° C., advantageously 100–300° C., and preferably about 200° C. In commercial size equipment external heating is not required except to expedite initiation of reaction and in some cases to maintain desired temperatures when a high flow rate of air is used. The temperature here is also advantageously maintained at 100–300° C., preferably about 200° C.

It has been found that the oxidation rate is considerably increased and the oxidation of residual elemental sulfur more completely effected at higher temperatures with several attendant advantages. For example the air reaction time of 6 hours at 120° C. is reduced to approximately 2 hours at 200° C. with nickel recoveries as good or better with the 200° C. oxidation as compared to 120° C. oxidation. Moreover any need for a post-oxidation hydrolysis step is eliminated with the 200° C. oxidation temperature. Furthermore, the more complete oxidation of the pulp at the higher temperature, including any residual sulfur that might be present, permits a subsequent direct cementation of the nickel without the expense of a solid-liquid separation or filtration.

Air is passed through the slurry at about 80° C. to 300° C. Air pressures of 60–500 p.s.i.g. are advantageously used. Agitation is advantageously used and this can be provided by impellers, etc., or by turbulence caused by the introduction of the gas.

With oxygen instead of air, similar temperatures are advantageously maintained, but since there is no diluent such as the nitrogen in the air which needs to be removed, the oxygen can be passed into the slurry with little or no through flow and 20–40 p.s.i.g. can conveniently be used.

The oxidation is continued until essentially all the sulfides have been consumed. This can be determined easily by analysis. However, probably the simplest indication of the progress of oxidation is the color of the reaction mass. The sulfidized material is black and as the oxidation progresses the color turns brown and eventually a yellow-tan color is approached which indicates essentially complete oxidation of the sulfides. The oxidized product has a pH in the range of 1.7–2.0.

As indicated in FIG. 2, the pH at this point is also an indication of the efficiency of nickel extraction. For example, in the extractions plotted in FIG. 2, 400 lbs. of sulfur were used per ton of ore. The pH range of 1.7 to 2 shows efficiencies of 87% to 70%, respectively.

The use of more sulfur shifts the pH curve to the left for a lower pH range indicating a more acid condition. This is probably due to the formation of greater amounts of iron sulfide which, as explained above, apparently is converted to sulfuric acid during oxidation.

It is believed that during the oxidaton step, the iron sulfide which has been formed simultaneously with the nickel sulfide is oxidized to form sulfuric acid. This sulfuric acid attacks residual magnesium and nickel silicates, thereby enhancing the extraction of nickel which may not have been converted to the sulfide form. Thus, some of the sulfur is used indirectly to make sulfuric acid in situ at much less expense than is involved in the direct use of sulfuric acid.

Attempts to prepare sulfuric acid in situ by the addition of iron sulfide or pyrites prior to oxidation proved unsuccessful. It is believed, therefore, that the iron sulfide

formed in situ is in a crystalline form or condition more susceptible to oxidation.

While applicants have certain theories as to how the reactions of this process proceed, they do not wish to be committed to such theories, but suggest them merely for better understanding of their invention.

For example, it is believed that the sulfidization of the nickel procedes according to the reaction:

$$3NnSiO_3+4S+4H_2O\rightarrow 3NiS+3H_2O+3SiO_2+H_2SO_4$$

The sulfuric acid formed as the byproduct in this reaction likewise aids the leaching operation. Sulfuric acid is also believed to be formed in the sulfur reduction of ferric oxide to ferrous oxide as follows:

$$3Fe_2O_3+S+H_2O\rightarrow 6FeO+H_2SO_4$$

Then additional sulfuric acid is believed to be formed by the reaction:

$$3FeO+7S+H_2O\rightarrow 3FeS_2+H_2SO_4$$

During the oxidation step the FeS_2 is apparently oxidized to form more sulfuric acid:

$$2FeS_2+2H_2O+7O_2\rightarrow 2FeSO_4+2H_2SO_4$$

and the nickel sulfide is apparently oxidized to nickel sulfate:

$$NiS+2O_2\rightarrow NiSO_4$$

From the above reactions it can be appreciated that a very inexpensive reagent, namely elemental sulfur is used in applicant's process to perform very efficiently an operation that was more expensively performed by sulfuric acid, caustic, etc. Furthermore, since this is a wet process the expensive predrying and high temperature operations of a pyrometallurgical operation are avoided.

There are a number of known methods by which the nickel can be removed from the nickel sulfate solution. For example, it can be precipitated as a nickel sulfide by hydrogen sulfide treatment of acidic solutions containing Ni, such as described in Patents Nos. 2,722,480 and 2,726,953. Less economically attractive is the method of neutralizing the solution to precipitate $Ni(OH)_2$.

From the nickel sulfide, the nickel metal can be recovered by hydrogenation or smelting by known pyrometallurgical or electrolytic methods.

The invention is best illustrated by the following examples. These examples are given merely for illustrative purposes and are not intended to limit in any way the scope of the invention nor the manner in which it can be practiced. Unless otherwise specifically indicated, parts and percentages here and throughout the specification are intended as parts and percentages by weight.

Example I

A crude Philippine Zone 4 ore containing 2.35% nickel, 0.1% cobalt, both predominantly in siiicate form, 17% iron and 13% magnesium, either in silicate or in magnesia form is ground in a ball mill for 30 minutes with sulfur (commercial grade) in sufficient amount to give a ratio of 400 pounds of sulfur per ton of crude ore, and with sufficient water to form a slurry having 35% solids content. Both the sulfur and the ore are ground to a particle size which in the dry sate will pass through a 200 mesh Tyler screen. About one liter of this slurry is weighed and placed in a 2-liter autoclave reactor made of 316 stainless steel and having a single impeller. The reactor is a standard one commercially available as Parr 2L Reactor 316SS. The slurry is diluted by water addition to a solids content of 30% and heated to a temperature of 225° C. Sufficient steam is released from the reactor to purge the air and then the temperature of 225° C. is maintained for a period of three hours. The autogenous pressure is 350 p.s.i.g. and agitator is operated at 625 r.p.m. At the end of the heating period the pH of the liquid phase of the slurry is 6.2.

The sulfidized product is diluted with water to 20% solids and transferred to a similar reactor equipped with a double impeller and an air inlet at the bottom of the reaction space. The temperature is maintained at approximately 100° C. for 6 hours with air being fed through the slurry under 150 p.s.i.g. at a rate of 2400 cc. per minute per 100 gms. of ore present. The color of the reaction mass when it is placed in the oxidizer is black and at the end of the oxidation it is a yellow-tan. The pH at the end of the oxidation is 1.8. The slurry product after cooling is flocculated with Separan, filtered, and the filter cake is given 6 washes with 50 cc. of water having a pH of 2.0. Analysis shows that 80.7% of the nickel is extracted from the ore, with 96.5% being accounted for in the extract and in the tailings and the balance apparently representing mechanical losses.

Example II

The procedure of Example I is repeated except that the oxidation is conducted at 120° C. for a period 5.7 hours and at the same air feed rate but at an air feed pressure of 143 p.s.i.g. The terminal pH is 1.7, the percent extraction is 85% and the accountability is 97.9%.

Example III

The procedure of Example I is repeated except that a sulfidization temperature of 235° C. and pressure of 430 p.s.i.g. are used, and in the oxidation step oxygen of approximately 100% concentration is used instead of air, with an oxidizing temperature of 110° C., and oxidizing period of 6 hours, an oxygen pressure of 40 p.s.i.g. and a flow through rate of 0. The percent extraction is 83.9%.

Example IV

The procedure of Example I is repeated twice except that the temperature during sulfidization is maintained at 235° C. and the amount of sulfur is varied, in one case using 200 lbs. per ton of ore and in the other case using 20 lbs. per ton of ore. In the test using 200 lbs. of sulfur the sulfidization time is 4 hours and in the other test it is 3 hours. The percent extraction of nickel with 200 lbs. of sulfur is 55.2%, and with 20 lbs. of sulfur extraction is only 13.2%.

Example V

The procedure of Example I is repeated except that a ratio 600 pounds of sulfur per ton of ore is used, and sulfidization is conducted at 235° C. and 430 p.s.i.g. for 3 hours. The air oxidation is conducted at 120° C. and 150 p.s.i.g. for 8 hours. The extraction of nickel is 92.1% and accountability is approximately 100%.

Example VI

The procedure of Example I is repeated twice using a similar ore to that of Example I and containing 2.33% nickel. In one case (A) 400 pounds of sulfur and in the other case (B) 375 pounds of sulfur are used per ton of ore. In test (A) grinding is conducted for 30 minutes and in test (B) 15 minutes with resultant terminal pH respectively of 7.3 and 7.1.

In each case the sulfidization is conducted with a slurry of 22% solids at a temperature of 235° C. for 3 hours at 430 p.s.i.g.

For each test the oxidation is conducted with air for 2 hours at a temperature of 200° C., a pressure of 400 p.s.i.g. and an air flow rate of 2400 cc./min. per 100 gms. of ore with the following results:

	(A)	(B)
Terminal pH after oxidation	1.05	1.8
Percent extraction, Ni	89.6	87.6
Percent accountability of Ni	95.0	95.5

While certain features of this invention have been described in detail with respect to various embodiments

thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A process for the extraction of nickel from a nickel-bearing ore of the silicate or oxide type comprising the steps of:
   (a) forming a water slurry containing finely divided sulfur and said ore in finely divided state, in a proportion of 150–800 pounds of sulfur per ton of ore, and having a pH of approximately 7,
   (b) heating said slurry in a closed reactor, and
   (c) maintaining the temperature of said slurry in said reactor in the range of 100–300° C. at a pressure of all of said sulfur has been reacted, and
   all of said sulfur has been reacted.

2. The process of claim 1 in which said reaction is effected for a period of at least 0.25 hour.

3. The process of claim 1 in which said reaction is conducted for a period of about 0.25–4 hours.

4. The process of claim 1 in which said reaction is conducted at a temperature of approximately 235° C. at approximately 450 p.s.i.g. for a period of about 2 hours.

5. The process of claim 1 in which said temperature is maintained at a range of 215–245° C. for a period of about 2–4 hours.

6. The process of claim 5 in which said sulfur is used in an amount of about 400 pounds per ton of ore.

7. The process of claim 1 in which said sulfur is used in an amount of 325–450 pounds per ton of ore.

8. A process for the extraction of nickel from a nickel-bearing ore of the silicate or oxide type comprising the steps of:
   (a) forming a water slurry containing finely divided sulfur and said ore in finely divided state, in a proportion of 150–800 pounds of sulfur per ton of ore, and having a pH of approximately 7,
   (b) heating said slurry in a closed reactor,
   (c) maintaining the temperature of said slurry in said reactor in the range of 100–300° C. at a pressure of at least 100 pounds per square inch until essentially all of said sulfur has been reacted, and
   (d) thereafter reacting the resultant slurry at a temperature of at least room temperature with an oxygen-containing gas until substantially all of the sulfide in said slurry has been oxidized.

9. The process of claim 8 in which said reaction with an oxygen-containing gas is at a temperature of at least 70° C.

10. The process of claim 8 in which said reaction with an oxygen-containing gas is at a temperature of about 100–300° C.

11. The process of claim 8 in which said reaction with an oxygen-containing gas is at a temperature of about 200° C.

12. The process of claim 8 in which said oxygen containing gas is concentrated oxygen.

13. The process of claim 8 in which said oxygen-containing gas is air.

14. The process of claim 13 in which said reaction with said oxygen-containing gas is at a temperature of about 100–300° C.

15. The process of claim 4 in which said temperature is about 200° C.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,365,341 January 23, 1968

Edward F. Fitzhugh, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 9, for "$3NnSi_3$" read -- $3NiSiO_3$ --; column 6, line 19, for "period 5.7" read -- period of 5.7 --; column 7, line 17, for "all of said sulfur has been reacted, and" read -- at least 100 pounds per square inch until essentially --.

Signed and sealed this 11th day of March 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents