

# Chemical Enrichment of Nickel Sulfide

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Received 14 November 2015; accepted 15 January 2016; published 18 January 2016

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## Abstract

The availability of polymetallic ores is getting leaner in grade and is larger but inferior in volumes than in the past, making the extraction of copper, nickel and other non-ferrous metals metallurgically more difficult to produce. The standard technologies, including enrichment and concentration, do not provide methods for obtaining monometallic concentrates and high extraction of metals into the commercial product. Pyrometallurgical processing of large volumes of poor raw materials is not economical and is complicated from the technological point of view. Conditions of chemical enrichment of poor natural materials have been studied with the use of technology of salt exchange leaching. The main impurity in sulfide ores of nonferrous metals is iron present in the forms of pyrite and pyrrhotite and the properties of chemical enrichment for nickel in pyrite concentrates has been investigated in this work. On the basis of thermodynamic analysis carried out with the use of Potential-pH Pourbaix's Diagrams, it has been established that, with the use of nickel salt, it is possible to leach iron sulfides from ores. Based on the study of the mechanism and kinetics of the process of dissolution of iron sulfides with nickel salts, it was established that during the dissolution, the chemical composition and thermodynamic characteristics of the dissolved iron sulfides change—the residues from leaching are enriched with iron sulfides that are rich in sulfur and also result with elemental sulfur formation. Enrichment of leaching residues with sulfide iron with increased sulfur content and formation on the surface of nickel sulfide leads to increase of diffusional resistances and the process is limited by the velocity of mass transfer. To increase the velocity of the process and completeness of the reaction, it is necessary to activate the process, in particular, by grinding the solid phase.

## Keywords

Nickel Sulfide, Pyrrhotite, Chemical Enrichment, Thermodynamics

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## 1. Introduction

Metallurgical processing involves more complex and poor ores now. Pyrite and pyrrhotite concentrates can be referred to such type of mineral raw materials with low content of non-ferrous metals, for example, nickel. In some pyrite concentrates of Kazakhstan, nickel content is at the level of 0.2% - 0.5%. Many ways of processing such kind of raw materials are developed. Most of them include melting of large volumes of raw materials accompanied with high energy expenses and significant loss of metal.

Previous thermodynamic analysis shows that sulfide concentrates with high iron content can be enriched with nickel taking into account differences of values in  $L_{P_{MeS}}$  ( $L_{P_{MeS}} = C_{Me^{2+}} \times C_{S^{2-}}$ ) of corresponding sulfides. Number of basic and technological investigations of nickel chemical enrichment of sulfide minerals has been carried out.

The process of chemical enrichment of sulfide concentrates containing nickel can be carried out either with application of selective iron leaching from original raw material or with transfer of the basic metals from ores into solution with further selective nickel precipitation. Many examples of technologies of sulfide materials leaching with transfer of nickel and basic iron mass into solution are described in literature. Autoclave oxidizing leaching has a great significance for processing of nickel containing mattes. Combined methods including processes of roasting and leaching are offered for processing of nickel-pyrrhotite concentrates. However, the high cost of processing and serious ecological problems didn't allow operating the enterprise for a long time.

Methods of oxidizing autoclave leaching were widely used in industry [1] [2]. In Norilsk, the process includes autoclave leaching of pyrrhotite concentrate with the subsequent cementation of nickel, cobalt and copper from the solutions with an iron powder. Methods of oxidizing autoclave leaching with the subsequent non-ferrous metals extraction from the solution with sorption or precipitation with hydrogen sulfide are being developed. The best results were obtained while applying hydrogen sulfide [3]. Technologies of matte application for collective precipitation of non-ferrous metals from solutions are also being developed [4].

On the basis of the technology developed in Gipronickel Institute (Leningrad), concentrates containing nickel pyrrhotite are melted at first for pyrrhotite matte, which is subjected to selective leaching with iron extraction into the solution and non-ferrous metals into a cake. For effective dissolution of sulfides with sulfuric acid, it is necessary to use an oxidizer for oxidizing of elemental sulfur produced in the process of direct sulphate leaching method [5]-[7].

Authors [8] have investigated a method of enrichment of valuable metals from sulfuric acid leach liquors of various nickeliferous oxide ores. Suitable enrichment processes based on sulfide precipitation and the Na-jarosite process have been tested and proved to be effective for recovering Ni, Co, and Cu from high-magnesium and high-iron pregnant liquors. Once the major impurities of magnesium and iron have been separated from the valuable metals, the resulting concentrated sulfate solutions mainly containing valuable metals (Ni, Co, and Cu) could be used for further metal recovery by solvent extraction methods. It is hoped that such sequences may also be applied for the recovery and enrichment of valuable metals from dilute pregnant leached liquors. According to Karbanee *et al.* [9] precipitation of  $Ni^{2+}$  was possible only when the  $H_2S$  (aq) sulfide species was available for reaction.

Thus, even the short review of processing methods of the poor concentrates containing nickel shows significant interest by the research as well as the extraction community in this problem. We studied the technology of processing of pyrite concentrates containing 0.2% - 0.5% of nickel. Earlier, the technology of the autogenous-pyrrhotinizing roasting of the pyrite concentrates was developed and the results were reported for the pyrrhotinized product where nickel is concentrated [10]. Simultaneously, the process of smelting of pyrite concentrate containing nickel for poor matte, with charging of oxidized nickel containing ores, was studied. The literature review and our research on collective dissolution of the pyrrhotinized products and poor mattes present viable and economical solutions. Nickel precipitation in the sulfide forms from solutions has been studied in this work.

## Thermodynamics of the Process

Thermodynamic analysis of precipitation of nickel sulfides from the water solutions of  $NiCl_2$  is carried out with construction of Potential-pH diagrams for Ni-S- $H_2O$  and Fe-S- $H_2O$  systems and with calculation of values of standard free energies and equilibrium constants of the principle reactions of Ni precipitation with hydrogen sulfide and ferrous sulfide (Table 1, Figure 1 and Figure 2).

Values of  $\Delta G^0$  and equilibrium constants show that nickel sulfide precipitation process with hydrogen sulfide in the presence of iron (reaction 1) and with iron sulfide (reaction 2) goes on sufficiently low- $\Delta G^0$  from -26.0 to

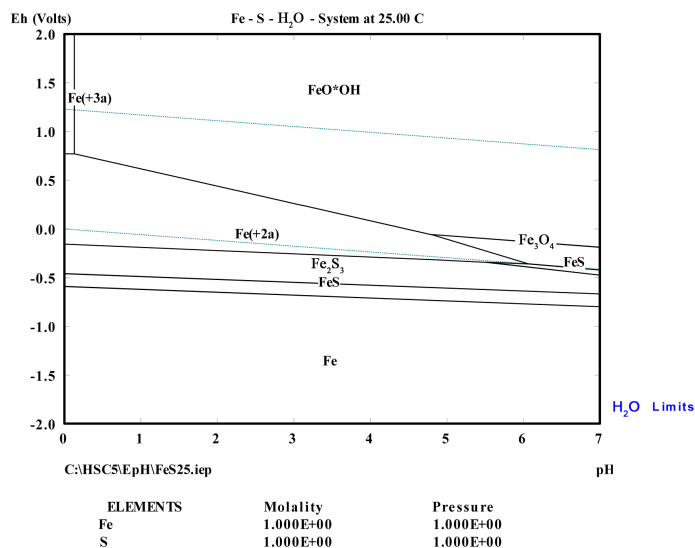


Figure 1. "Potential-pH" diagram for Fe-S-H<sub>2</sub>O system.

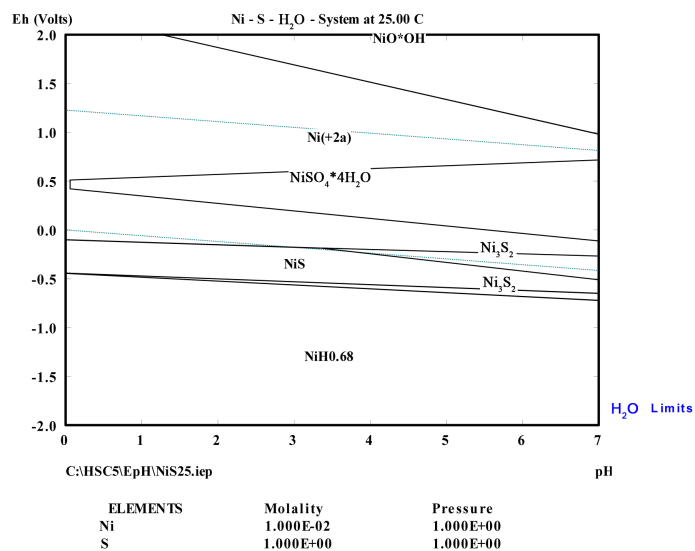


Figure 2. "Potential-pH" diagram for Ni-S-H<sub>2</sub>O system.

Table 1. Thermodynamic potential ( $\Delta G^0$ , kJ) and equilibrium constants of reactions.

№	Reaction	Temperature, K							
		293		313		353		373	
		$\Delta G^0$	LgK	$\Delta G^0$	LgK	$\Delta G^0$	LgK	$\Delta G^0$	LgK
1	$\text{NiCl}_2 + \text{H}_2\text{S} + \text{Fe} = \text{NiS} + \text{FeCl}_2 + \text{H}_2$	-94.8	16.9	-94.3	15.7	-93.2	13.8	-92.7	13.0
2	$\text{FeS} + \text{NiCl}_2 = \text{NiS} + \text{FeCl}_2$	-26.0	4.6	-26.2	4.4	-26.8	4.0	-27.0	3.8
3	$\text{Fe}_7\text{S}_8 + 7\text{NiCl}_2 = 7\text{NiS} + 7\text{FeCl}_2 + \text{S}$	-146.9	26.4	-149.3	24.9	-151.7	22.4	-152.9	21.4
4	$\text{NiCl}_2 + \text{Fe} = \text{Ni} + \text{FeCl}_2$	-42.7	7.6	-43.1	7.2	-44.1	6.5	-44.6	6.2
5	$\text{Fe}_2\text{S}_3 + 2\text{NiCl}_2 = 2\text{NiS} + 2\text{FeCl}_2 + \text{S}$	24.5	-4.4	23.9	-4.0	22.5	-3.3	21.7	-3.0
6	$\text{NiCl}_2 + \text{FeS}_2 = \text{NiS} + \text{FeCl}_2 + \text{S}$	31.1	-5.5	30.0	-5.0	27.8	-4.1	26.7	-3.7

–94.3 kJ/mol NiCl<sub>2</sub>, and equilibrium constant from 10<sup>4</sup> to 10<sup>16</sup>. It is worth mentioning that reaction of nickel cementation (reaction 4) can take place in the presence of elemental iron. However, thermodynamically, reaction of nickel sulfide creation in the presence of hydrogen sulfide and iron is more preferable to conduct according to reaction 1.

The “Potential-pH” diagrams (**Figure 1** and **Figure 2**) show that transfer into solution of Fe<sub>2</sub>S<sub>3</sub> requires higher oxidation potential than transfer into solution of FeS. Even under nickel concentration equal to 10<sup>–2</sup> g·mol/dm<sup>3</sup>, nickel sulfide is more stable in the water phase than FeS under concentration of 1 g·mol/dm<sup>3</sup>.

## 2. Experimental Methods

### 2.1. Materials, Methods and Equipment

#### 2.1.1. Precipitation of Nickel Sulfide with Hydrogen from Iron Solutions

Nickel precipitation was carried out from synthetic solutions containing 0.504 g/dm<sup>3</sup> of nickel and 182.0 g/dm<sup>3</sup> Fe (2+) in the glass reactor with a reverse fridge and mixer. pH of the original solution was 1.1. Composition of the solution corresponded to the solutions produced by leaching of the melted or thermochemically dissolved nickel bearing pyrite concentrate. Cast iron used for neutralization contained 96.8% of Fe and had a size of 0.15 mm.

The volume of the solution and velocity of the mixer rotation in all experiments was maintained at the same level. Grinding of solid phase was carried out with the help of glass balls loaded into the reactor. The cast iron charge was encapsulated into a glass ampoule and was loaded into the reactor and poured with the solution. After achieving necessary temperature the mixer was put into operation and was followed with hydrogen feeding. Time reading began after breaking of the ampoule.

The influence of the cast iron quantities on the degree of nickel precipitation at the temperature of 353 K was studied. We calculated the cast iron quantity on the basis of the amount of iron stoichiometrically necessary for neutralization of acid produced while nickel sulfide was being precipitated.

#### 2.1.2. Nickel Sulfide Precipitation from Thermochemically Dissolved Pyrite Concentrate

Precipitation was carried out from NiCl<sub>2</sub> solutions containing 518 mg/dm<sup>3</sup> of nickel. pH of the solution was 2.04. Thermochemically decomposed pyrite concentrate (pyrrhotinized product) was used in a vacuum precipitator. Its composition corresponded to the formulae Fe<sub>0.98</sub>S evidenced by x-ray analysis. There were three different pyrrhotite sub lattices found in the composition of the pyrrhotinized product. Precipitation was carried out in the glass reactor with cooling and a mixer with and without grinding of solid phase. Pyrrhotinized product was loaded into the retort in the encapsulated ampoules.

#### 2.1.3. Nickel Sulfide Precipitation with Matte

Nickel precipitation from iron bearing solutions with poor matte, with and without hydrogen sulfide, was conducted with a matte composition of (wt%): iron—71.6, nickel—3.1 and sulfur—24.3. Initial iron bearing solution had a concentration of (g/dm<sup>3</sup>) Ni—9.96 and, Fe (2+)—185.1.

## 3. Results and Discussion

Results in **Table 2** show that stoichiometrically necessary quantity of cast iron provides for almost full nickel precipitation. C<sub>Fe<sup>2+</sup></sub> : C<sub>Ni<sup>2+</sup></sub> ratio in the solution increases by 100 folds from 360 (in the original solution) to 36,000.

Results of the influence of precipitation temperature and duration on nickel behavior (**Table 3**) show that temperature increase significantly influences the precipitation velocity. Precipitation was carried out with the cast iron quantity at 5% excess over stoichiometry. Under temperature increase from 293 to 333 K for 60 minutes nickel correspondingly precipitated with 24.7% and 97.0% recovery. Temperature increase above 333 K and duration of the process in excess of 60 minutes didn't significantly influence nickel precipitation degree.

The following series of experiments was carried out with solutions containing 9.96 g/dm<sup>3</sup> of nickel and 185.1 g/dm<sup>3</sup> of iron (2+). pH of the solution was 0.9. Results in **Table 4** show significant influence of temperature on the indices of the process. Under temperature increase from 293 to 333 K, precipitation recovery increased from 44.1% to 87.4%. With increase of precipitation time up to two hours precipitation degree increased to more than 99%, following which further increase of the process duration increase of nickel concentration in solution took place.

**Table 2.** Influence of the cast iron quantity on nickel precipitation degree ( $\alpha$ , %) and nickel content in the solution ( $C_{Ni}$ , mg/dm<sup>3</sup>) from solutions containing 0.504 g/dm of nickel.

Cast iron quantity divisible by stoichiometrical	pH	$\alpha$	$C_{Ni}$	$C_{Fe^{2+}} : C_{Ni^{2+}}$ in solution
0.5	1.4	55.4	235	775
0.67	1.9	65.2	175	1040
0.83	2.0	89.6	52	3500
1.05	2.7	98.5	8	22750
1.17	3.5	>99	<5	>36,000
1.5	3.7	>99	<5	>36,000

**Table 3.** Dependence of nickel precipitation degree ( $\alpha$ , %) and nickel content in solution ( $C_{Ni}$ , ( $C_{Ni}$ , mg/dm<sup>3</sup>)) on the temperature and duration of precipitation from solutions containing 0.504 g/dm<sup>3</sup> of nickel (5% cast iron excess).

T, K	$\alpha / C_{Ni^{2+}}$ for precipitation time, minutes						
	5	10	15	30	60	120	240
293	3.4/487	4.6/481	6.8/470	13.0/440	24.7/378	58.4/208	82.9/86
303	4.9/479	10.2/452	18.5/411	26.4/367	45.7/272	70.3/150	90.0/50
313	10.6/450	18.4/411	26.8/369	46.9/266	72.0/140	87.5/64	95.9/21
323	20.1/403	33.5/335	48.3/261	73.6/133	87.2/63	93.6/32	97.8/11
333	38.7/309	62.4/189	77.1/115	91.9/40	97.0/15	98.2/9	98.9/5.5
343	41.1/297	65.4/174	79.3/104	93.6/38	97.2/15	98.4/9	98.9/5.5
353	45.6/275	70.3/150	83.9/81	96.0/21	97.9/11	98.5/8	99.0/5.5
363	48.0/262	82.7/87	85.9/71	98.0/10	99.0/5	99.3/3.5	99.3/3.5
378	-	-	-	-	-	99.6/2	99.6/2

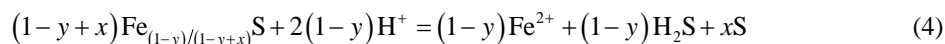
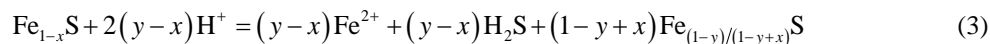
**Table 4.** Dependence of nickel precipitation degree ( $\alpha$ , %) and nickel content in solution ( $C_{Ni}$ , mg/dm<sup>3</sup>) on the temperature and duration of precipitation from solutions containing 9.96 g/dm<sup>3</sup> of nickel.

T, K	$\tau$ , min	Cast iron surplus	Ending pH	$\alpha_{Ni}$ , %	$C_{Ni^{2+}}$ , g/dm <sup>3</sup>	$C_{Fe^{2+}} : C_{Ni^{2+}}$ in solution	$C_{Ni} : C_{Fe}$ in the precipitate
363	120	0.0	1.05	3.0	9.93	18.6	0.8
»	»	0.67	1.25	71.3	2.86	66.7	5.15
»	»	0.83	1.50	84.9	1.5	126	4.4
»	»	1.05	2.10	>99	<0.1	>2000	6.7
»	»	1.17	2.80	>99	<0.1	>2000	3.34
»	»	1.5	3.60	>99	<0.1	>2000	1.5
»	»	1.87	3.95	>99	<0.1	>2000	0.9
363	30	1.05	1.15	53.1	4.67	40	0.23
»	60	»	1.85	92.0	0.8	237	0.29
»	120	»	2.10	>99	<0.1	>2000	6.7
»	240	»	2.10	98.5	0.15	1260	3.4
»	480	»	2.15	97.5	0.25	745	4.0
293	120	1.05	1.1	44.1	5.57	34	0.53
313	»	»	1.2	79.6	2.03	94	1.06
333	»	»	1.7	87.4	1.25	153	3.75
353	»	»	1.9	87.5	1.24	153	5.1
363	»	»	2.1	>99	<0.1	>2000	6.7
379	»	»	2.1	>99	<0.1	>2000	6.8

Mechanism of the chemical reaction of nickel precipitation with pyrrhotite and throilite is described by the following equations:



As it is seen from the obtained data in **Table 5**, nickel precipitation both with and without grinding, has no particular effect. Previously it was found that pyrrhotite is solution even in the non-oxidizing conditions takes place with formation of elemental sulfur:



Thus, while nickel sulfide precipitates on the surface of initial iron sulfide, it is enriched with iron sulfide of high sulfur content which is hard for dissolution in water. Alongside sulfur content increase in pyrrhotite, higher acidity of the solution is required and also higher oxidizing potential for its dissolution is needed. Extraction of elemental sulfur is also observed which stays on the surface of the reaction site and causes increase in the interior diffusion resistance. Besides, nickel sulfide by itself, while precipitating on the surface of the iron sulfide, creates additional diffusion resistance. The Pilling-Bed worth coefficient is seen to be equal for a pair FeS-NiS at 1.1. (Coefficient takes into consideration the ratio of the volumes of initial and extracted products). Microscopic analysis of obtained products indicate that the dense layer of the reaction products obtained from precipitation that covers the surface of iron sulfide hinders the effect of the process. In this case, it is clear that application of grinding increases the rate of the process and nickel precipitation degree. However, this index is much lower than the one in nickel precipitation with hydrogen sulfide with cast iron particles.

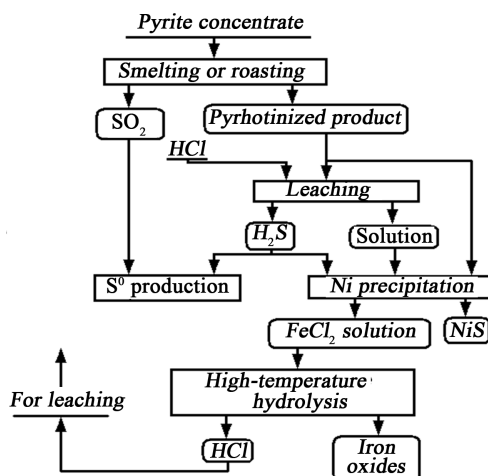
Results of nickel precipitation from ironless solutions in **Table 6** show that the process goes on to completion fully achieving 99% recovery practically without precipitator excess.  $C_{\text{Ni}}:C_{\text{Fe}}$  correlation in the precipitate is at the level of 5.0 - 5.5. Nickel precipitation with hydrogen sulfide in presence of matte (**Table 7**) was carried out

**Table 5.** Nickel precipitation results with pyrrhotitized product.

T, K	$\tau$ , min	Pyrrhotite excess treated by stoichiometric iron	With grinding		Without grinding	
			pH	$\alpha_{\text{Ni}}$ , %	pH	$\alpha_{\text{Ni}}$ , %
371	120	1.0	2.6	14.3	2.3	3.3
»	»	2.0	2.8	19.2	-	-
»	»	4.0	3.2	26.6	2.4	12.8
»	»	5.0	3.4	37.8	2.45	15.8
»	»	8.0	3.5	46.6	-	-
»	»	10.0	3.6	55.2	-	-
371	60	1.0	2.3	10.2	2.3	2.85
»	120	»	2.6	14.3	2.3	3.3
»	240	»	3.1	30.0	-	-
»	480	»	3.2	57.6	-	-
293	120	1.0	2.1	2.2	2.0	1.0
313	»	»	2.15	6.2	2.1	1.5
333	»	»	2.3	7.2	2.1	2.1
353	»	»	2.5	11.3	2.3	2.65
371	»	»	2.6	14.3	2.3	3.3

**Table 6.** Nickel precipitation with matte (Temperature is 80°C, duration-2 hours).

Pyrrhotite excess	pH	Content in solution, g/dm <sup>3</sup>		Degree of nickel precipitation, %	Content in precipitate, %		$C_{\text{Ni}}:C_{\text{Fe}}$ ratio in the precipitate
		Ni	Fe		Ni	Fe	
0.9	1.15	0.15	6.6	98.35	52.0	9.1	5.7
1.0	1.2	0.1	7.4	98.9	58.0	9.1	6.4
1.04	1.2	0.12	7.4	98.7	50.5	9.17	5.6
1.1	1.3	0.05	7.6	99.3	55.5	11.7	5.0
1.13	1.45	0.07	7.3	99.1	52.5	11.8	4.4
1.17	1.8	0.03	8.2	99.6	51.5	13.1	3.9



**Figure 3.** Flowsheet of chemical enrichment of pyrite concentrates with nickel.

**Table 7.** Nickel precipitation with hydrogen sulfide in the presence of matte (matte surplus coefficient is 1.05).

T, K	$\tau$ , min	pH	Nickel precipitation, %	$C_{Ni}:C_{Fe}$ ratio in the precipitate
293	120	1.3	27.45	0.45
313	120	1.6	65.2	1.87
333	120	1.8	97.1	4.5
353	120	2.0	97.4	3.8
363	120	2.0	98.7	4.1
379	120	2.0	99.8	4.0
379	30	1.0	24.7	0.32
379	60	1.3	43.3	1.1
379	90	1.95	70.5	3.5
379	240	2.0	99.8	3.0

and no difference was observed in comparison with precipitation without hydrogen sulfide. Temperature influence is observed, however. Almost complete nickel precipitation (98.7) is achieved at a temperature of 363 K.

#### 4. Summary

This research showed the possibility of chemical enrichment of sulfide concentrates with nickel while combining technologies that include smelting (or roasting) to produce pyrrhotinized product or matte, collective pyrrhotinized product or matte leaching and further selective nickel sulfide precipitation with metal pyrrhotinized product or matte as evidenced in [Figure 3](#).

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