

Preparation of Metallic Nickel Nugget from Lateritic Ore and Its Comparison with Synthetic Oxidic System

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Abstract— various processes have been established for extraction of nickel from lateritic ore. The hydrometallurgical routes are applicable to ore bearing nickel <2%, whereas pyro-metallurgical processes are adopted for ores with nickel > 2% depending on the content of nickel and gangue as well. In this paper, an attempt has been made to produce nickel enriched nugget from a mechanical mixture and a low grade nickel ore, using carbon as reductant in the presence of alkali chloride and sulphur. Experiments were carried out in 100gm scale with the mechanical mixture of pure nickel and iron sulphate and also with laterite ore samples. The raw materials used in the study, were dried at 110°C before mixing with carbon, alkali chloride and sulphur. The charge mix was transformed to a graphite crucible and roasted in a furnace at a predetermined temperature. After the reaction, the roasted mass was discharged in hot condition. It is observed that, the molten phase is separated from the gangue in the form of nugget at the bottom of the crucible. Role of alkali chlorides, carbon, sulphur, time of roasting and roasting temperature has been investigated during the study. The XRD, EPDX and microscopic analysis of the sample indicates that Ni, NiS are the major mineral phases present in the nugget along with Ni₃S₄ and Ni₃C as minor phases. An effort has been made for the enrichment of nickel using lateritic ore of Sukinda. It is observed that there is no clear cut separation of liquid mass from the ore charge. This may be due to the gangue minerals like silica, magnesium, calcium etc., present in the ore. Studies have further being carried out to establish the role of other minerals during the formation of nickel enriched nugget.

Index Terms—Nickel nugget, Segregation, pyro-metallurgical process, roasting, gangue.

I. INTRODUCTION

A significant deposit of nickel ore has been discovered in the Sukinda area of Orissa, India. The overburden has nickel content, ranges from 0.5-1.1%. Around 5,000,000t of such overburden is generated each year in addition to the 140,000,000t that has already been accumulated over several years of mining. It is estimated that rate of production may increase 10,000,000t/year, as the consumption chrome ore is increasing with time. In order to meet the recent industrial and technological growth, the demand of nickel is increasing equally. Thus, greater emphasis is now placed on the recovery of nickel from low grade oxidic ores. The nickel ferrous oxide ores are moist, low grade and virtually free of sulphur, copper (or) any precious metals except cobalt in minor quality. The

recovery of principal metal nickel, presents a different metallurgical picture compared to that for sulphide ores [1]. Many processes have been developed to treat these low grade ores out of which segregation roasting process is one of the processes that has been adopted by many researchers [2-3]. In this method, halogenating agents like NaCl, CaCl₂, MgCl₂ etc. are mixed with the ore along with reducing agents i.e. Coke, Charcoal, Coal etc. and the mixture is heated at about 900°C (or) above to carry out metallization reactions. The metals get segregated and collected on the carbon grains. These metals get separated easily by flotation (or) magnetic separation methods. Many processes have been tried [4-5] with varying the operating parameters to study the feasibility of the segregation reactions. An attempt has been made [6] to increase the nickel concentration during segregation using metallic iron as a reductant. By this method around 64.9% nickel metals could be obtained, using a garn iritic nickel ferrous ore. A study was undertaken to segregate nickel from oxidic ore in a rotary furnace, in which sufficient quantity of air is passed for combustion of charcoal to produce carbon monoxide gas. A maximum of 40-60% nickel could be segregated in the process [7]. A circulating reactor [8] was used to circulate the gas liberated by segregation roasting to facilitate chlorination's of the ore. In this method, nickel metallization was raised up to 78%. In some other attempts [9, 10] by increasing the temperature up to 1300°C, researchers were able to extract nickel more than 80%. It was observed that above 1200°C nickel forms a refractory material along with other silicates that hinders the nickel metallization. In another attempt, it has been observed that when the calcined ore is used as a charge material, an appreciable effect on nickel extraction could be found [11-13].

II. EXPERIMENTAL PROCEDURE

Experiments were carried out in 100g scale with pure nickel sulphate, iron sulphate as well as a mechanical mixture of pure nickel and iron sulphate and also with nickliferous lateritic ores. The raw materials used in the study were initially dried at 110°C before mixing. A calculated quantity of chloride salt and carbon was added to the ore/mechanical mixture, mixed thoroughly in a graphite crucible and the charge mix is subjected to roasting at a pre-determined temperature. The roasted material was discharged in hot condition over calcium oxide base. The molten mass was

separated from the gangue in the form of a nugget at the bottom. Effect of various parameters like percentage addition of alkali and alkaline earth metal chlorides, roasting temperature, moisture content and particle size etc. have been studied.

IV. RAW MATERIALS

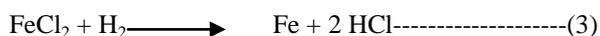
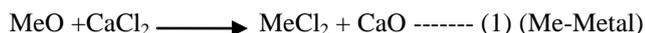
The raw materials used in the study are low grade limonitic lateritic ore and analaR grade nickel sulphate, iron sulphate, calcium chloride, sodium chloride and magnesium chloride etc. The composition of the charcoal used in the study composed of moisture 1.1%, volatiles 13.8%, ash 14.5% and fixed carbon 71.7%. The XRD study of the ore reveals that FeO(OH) is the major mineral. The chemical composition of the low grade limonitic lateritic ore is shown in Table-1.

Preparation of the Mechanical Mixture

The mechanical mixture was prepared by pulverizing the AnalA grade of nickel and iron sulphate in acetone medium, manually for 2 hours. The homogeneity of the sample was tested and used in the study.

V. THEORY AND CHEMICAL REACTIONS

Segregation roasting is an established technique to recover valuable metals from low grade oxidic ores and industrial wastes. In this process, the ore is reduced at high temperature, with a mixture of charcoal and chlorinating agent, to volatilize the metals in the form of chlorides. The volatilized metal chlorides get reduced by hydrogen to their metallic state and get segregated on the carbon grains. The metal formed is separated by means of flotation (or) magnetic separation to obtain a concentrate which is rich in metal values. The reactions involved are:



In the present study, nickel will be segregated in the form of nugget using sulphur. The use of sulphur helps in bringing down the melting temperature of the reaction mixture. Hence, at higher temperature sulphur along with nickel and iron forms a low melting metallic mass. The molten mass; thus formed get separated from the gangue and settled at the bottom of the crucible. It is then separated by pouring the molten mass over calcium oxide in hot condition. The reactions are:



VI. RESULT AND DISCUSSIONS

The experiments were carried out using mechanical mixture of pure nickel and iron sulphates, sulphated lateritic ore and raw lateritic ore. Role of operating parameters i.e. temperature, chlorinating agent, moisture, sulphur and the reducing agent have been studied.

Effect of Temperature

The temperature effect has been studied for a mechanical mixture between 850⁰C to 1200⁰C and the results obtained are given in Table-2. The data indicates that nickel metallization increases gradually with increase in temperature. It has been observed that for Set A (iron and nickel sulphate in the ratio of 1:1), the nickel metallization is comparatively more than for Set B (iron and nickel in the ratio of 49:1). In addition, Set A has less iron metallization than Set B which may be attributed to the liberation of hydrogen gas at higher temperature which reacts with atomic sulphur to produce H₂S and H₂O. The H₂O thus liberated dissolves the FeCl₂ formed during segregation and hence, there is a gradual increase in nickel metallization over iron. The Energy Dispersion (ED) spectra of the particulate are shown in the temperature range of 950⁰C to 1150⁰C. From the spectra, it is observed that with the rise in temperature, the metallic nickel concentrates more on the particulate. In this process, gradual desorption of metallic iron takes place and percentage sulphur remain uncharged (Table-3). This may be attributed to the formation of iron chloride, which catalyses the metallization reaction[9]. Analysis of the microscopic photographs of the segregated crystal reveals a eutectic of sulphur matrix embedded with distinct crystal phases. The phase has been identified as nickel and iron metal forming a metal cluster. With the gradual increase in temperature, metallic nickel gets concentrated in the crystal phase and there is a gradual fall in the iron value (Table-4). Finally, at around 1150⁰C, the nickel metallization reaches maximum with negligible amount of iron content. The microscopic photograph (Figure-1) indicates the gradual enrichment of nickel in the melt (nugget) with increase in temperature up to 1150⁰C [9].

Effect of Chlorination

Experiments were carried out with chloride salts of calcium, sodium and magnesium in the range of 5-15 wt%. The results obtained are shown in Table-5. It is observed that CaCl₂ showed better result on nickel metallization in comparison to other salts. The reaction of water vapor with CaCl₂ is represented as follows:-



From the above reaction (9) it is observed that in situ moisture liberated at higher temperature reacts with the CaCl₂ to form CaO and HCl gas. The CaO, thus, formed acts as a flux to remove gangue minerals, enriching nickel in the molten mass.

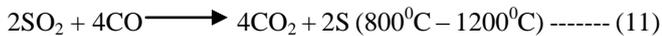
Role of Moisture

The moisture plays a significant role on segregation of nickel and the results are shown in Table-6. The data reveals

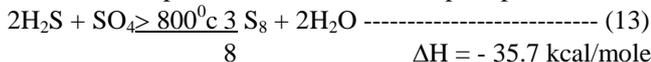
that the calcined material shows better yield in comparison to the charge heated directly at 1000°C. The higher metallization rate of calcined sample may be due to the complete removal of the moisture [6]. The moisture thus released, reacts with the chlorinating agent to form hydrogen chloride gas. The hydrogen chloride gas formed; react with the oxides to form respective chlorides. In direct reduction at 1000°C there may be partial conversion of nickel chloride due to incomplete reaction of CaCl₂ with water vapor. The metallic iron formed during reduction eq(6) reacts with NiCl₂ to replace nickel by iron, forming iron chlorides.



During this process, metal sulphates decompose to respective oxides liberating SO₂. The SO₂ thus liberated, reacts with CO gas (11) available in situ, forming molten sulphur and liberating CO₂ gas.



The molten sulphur reacts with insitu H₂ to form molten H₂S (H). The molten H₂S has a tendency to absorb an appreciable quantity of SO₂ and FeCl₂ (12, 13). During the reaction decomposition of Fe₂(SO₄)₃ takes place leads to the formation of porous catalyst like charcoal and Fe₂O₃. The molten H₂S reacts with the sulphur dioxide left inside the reaction atmosphere to form a molten sulphur phase.



$$\Delta H = - 35.7 \text{ kcal/mole.}$$

The fine particulates of metallic iron and nickel get embedded in the molten sulphur phase forming a liquidated metal enriched mass that solidifies to a metallic nugget at room temperature. The XRD data of the nugget obtained from NiSO₄, Fe₂(SO₄)₃ and its mechanical mixture are shown in Table-7.

Particle Size Effect

Particle size effect has been studied in the range of – 0.106 mm to 8 mm and the results are incorporated in Table- 8. It is seen that finer particles have shown higher metallization in comparison to courser particles. This may be attributed to the following reasons:

- Availability of large surface areas and porosity.
- The reaction is not hindered due to the formation of product layer and hence, metallization is much faster.
- More tendencies to form the eutectic mixture with finer particles.

Lateritic Ore

Experiments were carried out at optimum conditions using limonitic lateritic ores. The results obtained are shown in Table-9. It is found that with lateritic ore there is no clear separation of metallic phase or nugget formation. But during segregation production of a remarkable metallic concentrate is noticed. The crystal phases are analyzed and the data are

represented in Table-9. The microscopic photographs of phase A and B indicates that the crystal phase becomes voluminous with the raise in temperature and at around 1250°C a clear crystal phase is formed, with 41.8% metallic nickel 39.43% Fe using 10 wt% CaCl₂ and charcoal each.

Sulphated Lateritic Ore

Similarly, experiments were carried out with sulphated lateritic ore (using elemental sulphur with ore). The sulphated ore was subjected to segregation experiments to get metallic nickel. It is observed that there is no clear cut separation of metallic nugget (Figure-2). It may be due to the fact that the gangue mineral present in the ore might have reacted with the elemental sulphur to form complex sulphides and thus, inhibiting the formation of a metal enriched molten mass.

VII. CONCLUSION

Nickel could be enriched in the form of metallic in the presence of alkali chloride and sulphur nugget from a synthetic mixture of iron and nickel where carbon is added as a reductant. The XRD of the mechanical mixture indicates nickel and iron as major phases where as Ni₃S₄, Ni₃C and Fe₃C as found to be the minor phases. Calcination at 800°C prior to segregation improved the metal extraction. It is possible to proceed up to 92% nickel metallization with 45% iron from the mechanical mixture at 1150°C, where 10 wt% of charcoal and calcium chloride have been added. No clear molten metallic mass could be obtained using lateritic ore and its sulphated sample.

VIII. ACKNOWLEDGMENT

The preferred spelling of the word “acknowledgment” in American English is without an “e” after the “g.” Use the singular heading even if you have many acknowledgments. Avoid expressions such as “One of us (S.B.A.) would like to thank” Instead, write “F. A. Author thanks” Sponsor and financial support acknowledgments are placed in the unnumbered footnote on the first page.

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Table-1: Chemical analysis of the chromitiferous overburden (-106µ)

Constituents	Percentage
Moisture	1.50
Fe ₂ O ₃	66.58
Ni	1.31
Co	0.078
SiO ₂	5.60
CaO	4.65
Al ₂ O ₃	4.85
MgO	2.51
Acid In	1.50
LOI	12.12
Total	99.888

Table-2: Effect of Temperature

**Conditions: Set A: Fe₂(SO₄)₃ + NiSO₄ = 50g (1:1)
Set B: Fe₂(SO₄)₃ + NiSO₄ = 50g (49:1)
CaCl₂ = 10 wt%, Charcoal = 10 wt%,
Time=1hr.**

Temperature in °C		Set A		
Set B				
	% Ni Met	% Fe Met	% Ni Met	% Fe Met
850	36.81	10.44	29.43	12.14
900	49.92	13.09	44.32	18.98
950	69.76	19.23	61.99	23.23
1000	78.52	25.81	67.98	31.58
1050	83.09	30.47	77.04	36.77
1100	89.01	36.79	81.88	52.42
1150	92.79	45.55	85.09	63.89
1200	96.88	59.78	88.79	75.00

Table-3: Data analysis of ED Spectra

Element in wt%	Spectra A (950°C)	Spectra B (1050°C)	Spectra C (1150°C)
Fe	26.43	2.64	----
Ni	51.44	75.23	75.88
S	22.03	22.13	24.12

Table-4: Microscopic analysis of segregated crystal phase
**Conditions: CaCl₂ = 10 wt%, Charcoal = 10 wt%
Fe₂(SO₄) + NiSO₄ = 50g (1:1), Time = 1hr**

Temperature in °C			Phase A	
Phase B				
	% Ni Met	% Fe Met	% Ni Met	% Fe Met
950	71.0	27.8	71.3	28.7
1050	89.9	10.0	90.4	9.1
1150	96.8	2.7	98.3	1.4

Table-5: Effect of alkali chlorides

**Conditions: Fe₂(SO₄)₃ + NiSO₄ = 50g (1:1)
Charcoal = 10 wt%,
Temperature = 1100°C, Time=1hr**

Salts	5wt%		10wt%		15wt%	
	% Ni Met	% Fe Met	% Ni Met	% Fe Met	% Ni Met	% Fe Met
CaCl ₂	80.4	48.1	88.1	50.79	89.47	50.98
NaCl	74.7	32.44	81.43	43.43	82.08	45.5
MgCl ₂	75.98	35.73	82.78	40.77	83.89	49.9

Table-6: Nickel metallization in calcined and directly heated samples

Sample A = Heated directly at 1000°C
**Conditions: Fe₂(SO₄)₃ + NiSO₄ = 50g (1:1)
CaCl₂ = 10wt%, charcoal=10wt%**

Sample B = Calcined at 800°C for 2hrs and heated continuously up to 1000°C to undergo roasting
**Conditions: Fe₂(SO₄)₃ + NiSO₄ = 50g (1:1)
CaCl₂ = 10wt%, Charcoal=10wt%,
Time:1hr**

Samples	% Ni Met	% Fe Met
A	68.4	26.01
B	80.32	24.88

Table-7: XRD data of the segregated samples

**Conditions: Temperature=1000°C,
Time: 1hr, CaCl₂=10wt%
Charcoal= 10wt%, Sample wt. =50g.**

Samples	Major phase	Minor phase
Fe ₂ (SO ₄) ₃	Fe, FeS	Fe ₃ C ₂ , Fe ₅ C ₂
NiSO ₄	Ni, NiS	Ni ₃ S ₄
Fe ₂ (SO ₄) ₃ + NiSO ₄	Ni, Fe	Ni ₃ S ₄ , Ni ₃ C, Fe ₃ C

Table-8: Effect of particle size

**Conditions: Temperature = 1100°C, CaCl₂= wt%,
carbon= 10wt%
NiSO₄ + Fe₂(SO₄)₃ = 50g (1:1), Time:1hr
(All the samples are calcinated at 800°C and then heated continuously at the particular temperature)**

Size	% Ni Met	% Fe Met
-0.106 mm	94.32	35.48
-0.5 mm	88.85	32.79
-2 mm	82.01	29.41
-4 mm	75.99	28.98
-8 mm	64.01	29.04

Table-9: Study using lateritic ore

**Conditions: Temperature= 1150°C, CaCl₂= 10wt%,
Charcoal= 10wt%, Sample= 50g, Time: 1hr,
Sample A= Lateritic ore**

Sample B= Lateritic ore + Sulphur 25wt%

Sample C= Sulphated lateritic ore

Sample	% Ni Met	% Fe Met
A	72.83	9.04
B	74.31	12.43
C	78.22	13.49

Met = Metallisation

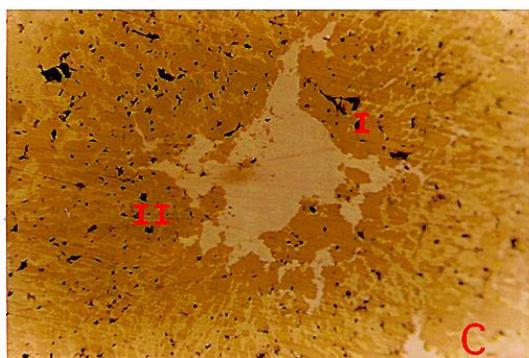
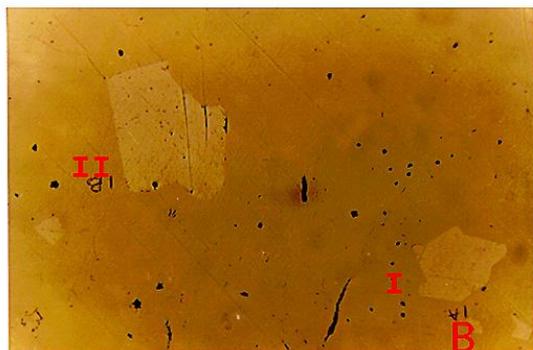
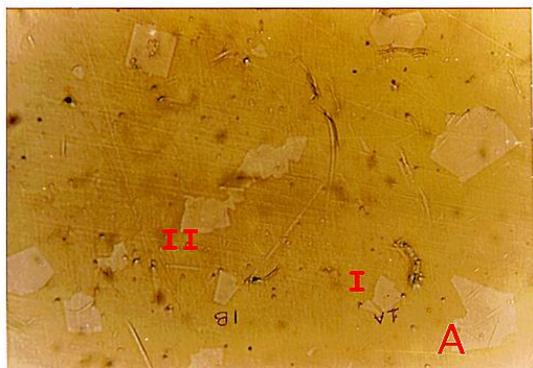


Fig-1 Microphotographs of the segregated crystals embedded with Sulphur at different temperatures

A.950°C B.10500C C.11500C

Conditions: Time=1hr, $Fe_2(SO_4)_3 + NiSO_4 = 50g (1:1)$, $CaCl_2 = 10wt\%$, Charcoal=10wt

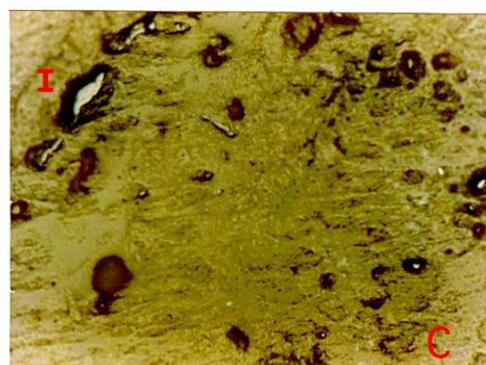
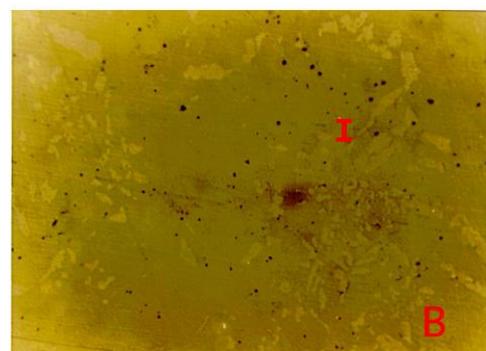
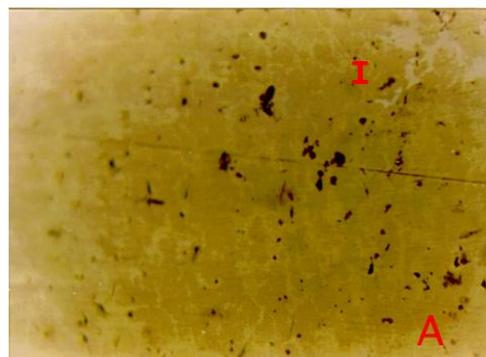


Fig-2 Microphotographs of segregated crystal phase

A. Lateritic ore, B. Lateritic ore with sulphur (25wt%), C. Sulphated lateritic ore

Conditions: Temp.=1150°C, $CaCl_2 = 10wt\%$, Charcoal=10wt%, Time=1hr.

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