A comparative study of different leaching processes for the extraction of Cu, Ni and Co from a complex matte

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Abstract—The extraction behaviors of Cu, Ni and Co from a complex matte under different leaching conditions have been discussed. The synthetic Cu-Ni-Co-Fe-S matte was prepared by melting the pure metals. The matte contained 24.95% Cu, 35.05% Ni, 4.05% Co, 11.45% Fe, 24.5% S, similar composition as is expected to be obtained by reduction smelting of the Pacific Ocean nodules followed by sulphidisation of the alloy. The different phases identified are $CuFeS_2$, CuS_2, $(FeNi)_9S_8$, $(FeNi)S_2$, Ni_9S_8, Ni_3S_2, $(CoFeNi)_9S_8$ and Co metal. The merits and demerits of each process of dissolution i.e., H_2SO_4/oxygen pressure leaching, atmospheric $FeCl_3$ leaching, $NH_4OH/(NH_4)_2SO_4$ pressure leaching are discussed in detail. Out of the three, the H_2SO_4/oxygen pressure leaching process is found to be the most suitable with more than 99% metal extraction efficiency within 1 h of leaching time. From the X-ray diffraction analysis, the different undissolved phases corresponding to different leaching processes have been identified. The metal extraction efficiency decreased in case of atmospheric $FeCl_3$ leaching and $NH_4OH/(NH_4)_2SO_4$ pressure leaching processes due to the formation of product layer such as elemental sulfur and goethite, respectively.

Key words: Manganese Nodules, Matte, H_2SO_4 Pressure Leaching, $NH_4OH/(NH_4)_2SO_4$ Pressure Leaching, Atmospheric $FeCl_3$ Leaching

INTRODUCTION

Deep-sea manganese nodules are one of the most important minerals discovered in the recent past, which have very high potential as a source of non-ferrous metals such as copper, nickel, cobalt and manganese. As the land-based resources of these valuable metals are either inadequate or depleting fast, the possible exploitation of sea bed manganese nodules has gained much importance, particularly in the Korean context where there are almost no primary resources of these metals. The vast size of these deposits, for example, of the order of 10^{11} ton in the Pacific Ocean, is the main reason for the continued research and development [1]. Though the economic potential of recovering valuable metals from nodules has long been recognized, an economically viable as well as environmental friendly extraction process is yet to be developed.

Sea nodules are comprised mainly of oxides of manganese and iron together with various valuable metals such as copper, nickel and cobalt [2,3]. These metals are present in oxide form and are reported to be in the lattices of iron and manganese minerals [4,5]. Therefore, breaking up of these lattices by pyrometallurgical reduction or hydrometallurgical reductive dissolution is an important step for the satisfactory recovery of valuable metals. The extraction processes developed so far for sea nodules fall mainly under two categories: pyrometallurgical pre-treatment followed by hydrometallurgical processing and purely hydrometallurgical processing. Some pyrometallurgical pre-treatments are smelting, reduction-roasting, sulfatizing, chloridizing, etc. [6-10]. The reductive dissolution is performed by leaching in hydrochloric acid, sulfuric acid, ammonia, etc., in

absence or presence of reducing agents such as sulfur dioxide, pyrite, sodium sulfide, charcoal, alcohol, organic acids etc. [11-15]. Based on literature and contacts with industry [16], the most promising leaching systems for commercialization have been identified as (1) sulfuric acid/oxygen, (2) ferric chloride, and (3) ammonia/oxygen. Each method has its own merits and demerits. The sulfuric acid/oxygen system has good potential for commercialization; however, the kinetics is relatively slow at typical in-situ conditions. To enhance metal extraction rate, it needs to be operated at high pressure and temperature conditions. Although the ferric chloride system shows promise, severe corrosion problems have resulted in limited industrial interest. By contrast, the ammonia/oxygen system has some unique advantages which make it of more interest to industry. The advantages are that the basic leach solution alleviates several corrosion problems observed with the acidic systems and cleaner leach liquors produced, thus facilitating subsequent metal recovery [17]. However, similar to sulfuric acid/oxygen system, it has the disadvantage of operating at relatively high temperature and pressure.

The Minerals and Materials Processing Division of the Korea Institute of Geoscience and Mineral Resources (KIGAM), Korea has been working for the past several years on the processing of the Pacific Ocean manganese nodules for metal recovery. A process based on pyrometallurgical pre-treatment of nodules followed by hydrometallurgical processing has been proposed by KIGAM and it involves the pyrometallurgical smelting reduction-sulfidation route to produce Cu-Ni-Co-Fe rich matte and Mn slag [18], followed by leaching with suitable reagents [19-21]. In the present paper we have made a comparison study of three different leaching processes (H_2SO_4/oxygen pressure leaching, atmospheric $FeCl_3$ leaching, $NH_4OH/(NH_4)_2SO_4$ pressure leaching) carried out in our laboratory to recover valuable metals like Cu, Ni and Co from Cu-Ni-

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Co-Fe rich matte.

EXPERIMENTAL

The synthetic Cu-Ni-Co-Fe matte having similar composition as is expected to be obtained by reduction smelting of the Pacific Ocean nodules followed by sulfidization of the alloy was prepared by melting the pure metals in required proportions in an induction furnace. A graphite crucible was used for this purpose. Appropriate amount of metals placed in the crucible was heated to about 1,500 °C. When the alloy was completely melted and homogenized, sulfur addition was made. To avoid loss due to evaporation, pure sulfur powder was compacted into small cylinders in a mechanical press and manually held into the melt and stirred with a graphite rod. At the end of the run, the crucible was removed from the furnace and cooled to room temperature. The matte was crushed in a jaw crusher, ground in a ball mill and sieved under 100 μm for further study.

The pressure leaching experiments were carried out in a 450 ml capacity autoclave (Model 4562, PAR, USA) with 100 ml of leach solution and the desired amount of matte. Temperature was controlled through a PID controller with digital read-out for temperature, pressure and agitation speed. The contents were heated to the desired temperature. On attainment of temperature, the contents were stirred at 600 RPM and oxygen was introduced into the system continuously to maintain a constant pressure during the entire period of the experiment. Reaction time was counted after the introduction of oxygen into the reactor. The atmospheric $FeCl_3$ leaching experiments were performed in a glass reactor, with a Teflon cap in the central hole in which the axis of a Teflon stirrer with adjustable revolutions was placed. The flask was heated by an electrical heating mantle fitted with a temperature controlling thermostat where the variation of temperature was ±1 °C. The sulfur content in the carbon tetrachloride was determined by weighting the residue after evaporation of the solvent at a low temperature under vacuum using a rotavapor (Buchi, R-134). Each leaching experiment was performed at 5% (w/v) pulp density of matte. The contents were cooled, discharged, filtered and analyzed by atomic absorption spectrophotometer (AAS, Varian, Spectr-400) after suitable dilution. The residues were washed, dried in an air oven at 110 °C for 24 h. Known amounts of residues were acid digested and analyzed for Cu, Ni, Co, and Fe. In each case a satisfactory (±3%) material balance was obtained. Particle size measurements were done by a Malvern particle size analyzer (Hydro 2,000 M/MU). The mineralogical composition of the matte before and after leaching was carried out by X-ray diffraction analysis (XRD, Rigaku, Model-RH 200, Japan) at a scanning speed of 2 deg/min using Cu-Kα radiation source. The identification of mineral phases was based on d-values and integrated intensities. The surface area of the matte was determined by BET method using five-point surface N_2 (Micromeritics, Model - TriStar, V 5.02, USA). Sulfur analysis was done by a LECO SC-432 analyzer. A scanning electron microscope (SEM, JEOL, JSM-6380LA) was used for particle observation in the matte before and after leaching.

RESULTS AND DISCUSSION

1. Characterization of the Matte

Table 1. The average particle size distribution of the matte

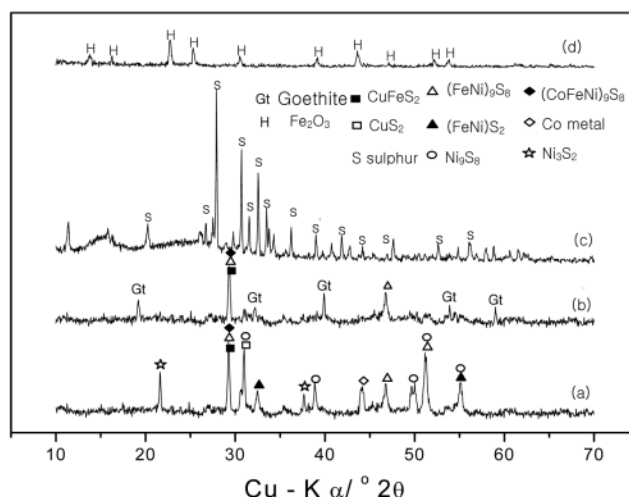| Particle size (μm)	Distribution (wt%)
−100+63	25.9
−63+25	66.9
−25	7.2

Fig. 1. XRD pattern of matte and leached residues under best leaching conditions, (a) matte, (b) 2 M NH_4OH+2 M $(NH_4)_2SO_4$, 15 kg/cm² pressure, 200 °C and 1 h, (c) 1.5 M $FeCl_3$, 0.3 M HCl, 90 °C and 7 h, (d) 1.0% H_2SO_4, 150 °C, 10 kg/cm² and 1 h.

The chemical analyses of the synthetically prepared Cu-Ni-Co-Fe matte contained 24.95% Cu, 35.05% Ni, 4.05% Co, 11.45% Fe, and 24.5% S. It is established that hydrometallurgical processes, particularly pressure leaching processes, are sensitive to particle size. So in the present study we reduced the particle size below 100 μm prior to processing by pressure leaching. Table 1 shows the particle size distribution of the bulk sample used in the study. About 67% of the sample was in the range −63+25 μm. Specific surface area of the matte was found to be 0.694 m²/ gm. The X-ray diffraction pattern of the matte is shown in Fig. 1a. The major mineral phases identified were: $CuFeS_2$, CuS_2, $(FeNi)_9S_8$, $(FeNi)S_2$, Ni_9S_8, Ni_3S_2, $(CoFeNi)_9S_8$ and Co metal. There was no peak for elemental sulfur indicating proper reaction with the metal ions with elemental sulfur.

2. Chemistry of Different Leaching Processes

It is well known that metal oxides dissolve rapidly in acids compared to sulfides. To enhance the sulfide dissolution the presence of an oxidant is required. Ferric ion is one such oxidizing agent, used successfully for the dissolution of mineral sulfides. The solution must be acidic since ferric hydroxide starts to precipitate at about pH 3. The leaching of complex Cu-Ni-Co-Fe matte in presence of $FeCl_3$ can be described by the general equation:

$$MS+2Fe^{3+}=M^{2+}+S^{o}+2Fe^{2+} \tag{1}$$

where, M stands for Cu, Ni and Co.

The rate of dissolution of sulfides in presence of Fe^{3+} ion is controlled by chemical reaction rather than diffusion processes. The oxidation potential of ferric chloride leaching system results in ele-

Table 2. Effect of different leaching parameters on the extraction of metals using atmospheric FeCl₃ leaching process
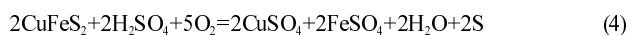
Time, h	[FeCl₃], M	[HCl], M	Temp., °C	CCl₄, g	Extraction of Cu, %	Extraction of Ni, %	Extraction of Co, %
1.0	1.0	0.3	90	-	90.5	55	39
3.0	1.0	0.3	90	-	98	82	57
5.0	1.0	0.3	90	-	98.8	90.5	61
7.0	1.0	0.3	90	-	99	91	64
7.0	0.5	0.3	90	-	80	61	29
7.0	1.0	0.3	90	-	99	91	64
7.0	1.5	0.3	90	-	99.5	93	85
7.0	2.0	0.3	90	-	99.9	95	87
7.0	1.5	0.1	90	-	98.7	88	79
7.0	1.5	0.3	90	-	99.5	93	85
7.0	1.5	0.5	90	-	99.5	95	86
7.0	1.5	0.3	30	-	60	31	16
7.0	1.5	0.3	50	-	70	55	45
7.0	1.5	0.3	70	-	82	82	75
7.0	1.5	0.3	90	-	99.5	93	85
7.0	1.5	0.3	30	100	63	35	18
7.0	1.5	0.3	50	100	82	61.5	50
7.0	1.5	0.3	70	100	94	91	82

mental sulfur as one of the major by-products, a form generally more acceptable environmentally than the SO_4^{2-} from H_2SO_4 and ammoniacal pressure leaching. Iron can be rejected as a precipitate, e.g., goethite or jarosite.
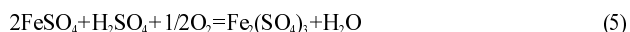
Hot concentrated H_2SO_4 is another oxidizing agent. The oxidizing power may be considered by the result of SO_3 decomposition as follows:

$$H_2SO_4 = H_2O + SO_3 \tag{2}$$

$$SO_3 = SO_2 + 1/2O_2 \tag{3}$$

However, leaching with dilute H_2SO_4 at ambient temperature and pressure is a slow process in which acid consumption is high and the final extraction of valuable metals may be incomplete. To improve the extraction of the valuable nonferrous metals, another oxidizing agent in the form of oxygen has been used successfully. Metals are leached in form of soluble metal sulfides. A typical example of $CuFeS_2$ is presented below:

$$2CuFeS_2 + 2H_2SO_4 + 5O_2 = 2CuSO_4 + 2FeSO_4 + 2H_2O + 2S \tag{4}$$

Depending on the acid concentration, pH and temperature the ferrous sulfate would get oxidize to ferric sulfate, which at about 100 °C hydrolyzes rapidly, even at a pH as low as 1.5, to hematite as shown in the following reactions:

$$2FeSO_4 + H_2SO_4 + 1/2O_2 = Fe_2(SO_4)_3 + H_2O \tag{5}$$

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4 \tag{6}$$

The combination of ammonia and ammonium salts is known to be a powerful lixiviant used in hydrometallurgical processes. Many metals including Cu, Ni and Co can be extracted by using a mixture of ammonia and ammonium salts under high temperature and pressure conditions. The detailed chemistry of the oxidative ammonia leach is quite complex and multi step, but the basic principles are reasonably established [22]. Briefly, the sulfide component

is oxidized to a soluble species, predominantly sulfate (SO_4^{-2}) together with some lower oxidation state species such as thiosulfate ($S_2O_3^{-2}$), thionate ($S_3O_6^{-2}$) and sulfamate ($NH_4 \cdot SO_3 \cdot NH_2$). The Fe component is oxidized to the +3 state and precipitated as hydrated ferric oxide ($Fe_2O_3 \cdot H_2O$). The Cu and Ni are released in the +2 oxidation state and stabilized in solution by the formation of amine complexes with NH_3 ligands. On the other hand, cobaltic ammine complexes are more stable compared to cobaltous ammine in the higher pH range.

2-1. Atmospheric FeCl₃ Leaching

The effect of FeCl₃ and HCl concentrations, temperature and addition of CCl₄ on metal extraction are discussed in this section (Table 2). Using 1.0 M FeCl₃ and 0.3 M HCl, the fraction of Cu, Ni and Co dissolved into solution was studied up to 7 h reaction time at 90 °C. The results clearly demonstrated that Cu dissolution was fast and reached equilibrium within 3h compared to Ni and Co, which needs 5 h and 7 h, respectively. Effect of FeCl₃ concentration showed that, by using 0.5 M FeCl₃ almost 80% Cu was leached out to the solution within 7 h. With further increasing FeCl₃ concentration to 1.0 M and above showed more than 99% extraction of Cu within that period. The effect of FeCl₃ concentration on Ni extraction was almost similar to Cu extraction. Whereas, Co extraction was slow and reached maximum 87%, even though FeCl₃ concentration was increased to 2.0 M. In 7 hrs time, about 99% Cu, 93% Ni and 85% Co could be leached out using 1.5 M FeCl₃ and 0.3 M HCl.

Fig. 2 shows the leaching efficiency of Cu, Ni and Co using HCl (0.1, 0.3 and 0.5 M) and mixture of HCl-FeCl₃ at 90 °C and 7 h. The main aim of carrying the leaching experiments in two different conditions was to distinguish the effect of FeCl₃ and HCl, individually. It was found that Cu extraction was almost negligible in all the three concentrations of HCl studied. Whereas, in the presence of 1.5 M FeCl₃, extraction of Cu was more than 99% at 90 °C and 7 h. This showed that FeCl₃ was solely responsible for the extraction of total Cu. Both Ni and Co showed similar extraction be-
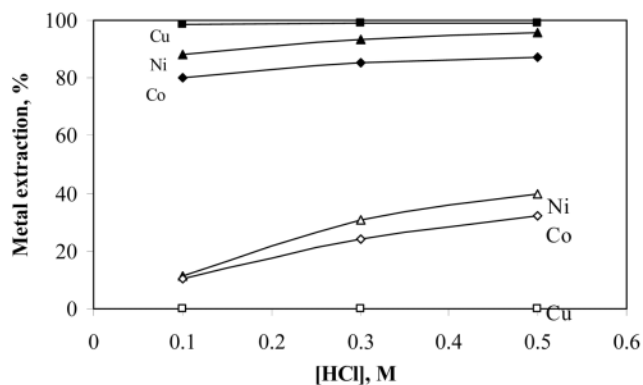
Fig. 2. Effect of HCl concentration (open marks) and HCl+FeCl₃ (closed marks) on the extraction of metals (FeCl₃=1.5 M, Temp=90 °C, Time=7 h).
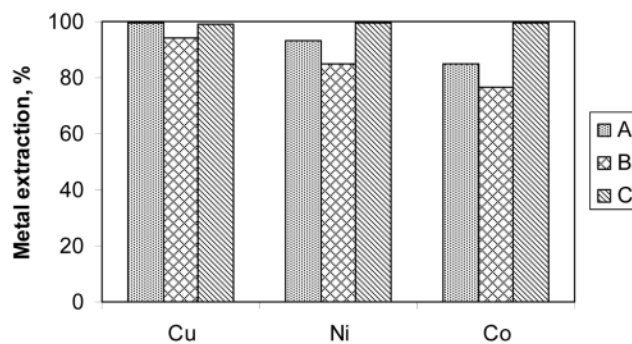

Fig. 3. Cu, Ni and Co extraction efficiency under best conditions of different leaching processes (A=atmospheric FeCl₃ leaching, B=NH₄OH/(NH₄)₂SO₄ pressure leaching, C=H₂SO₄ pressure leaching).
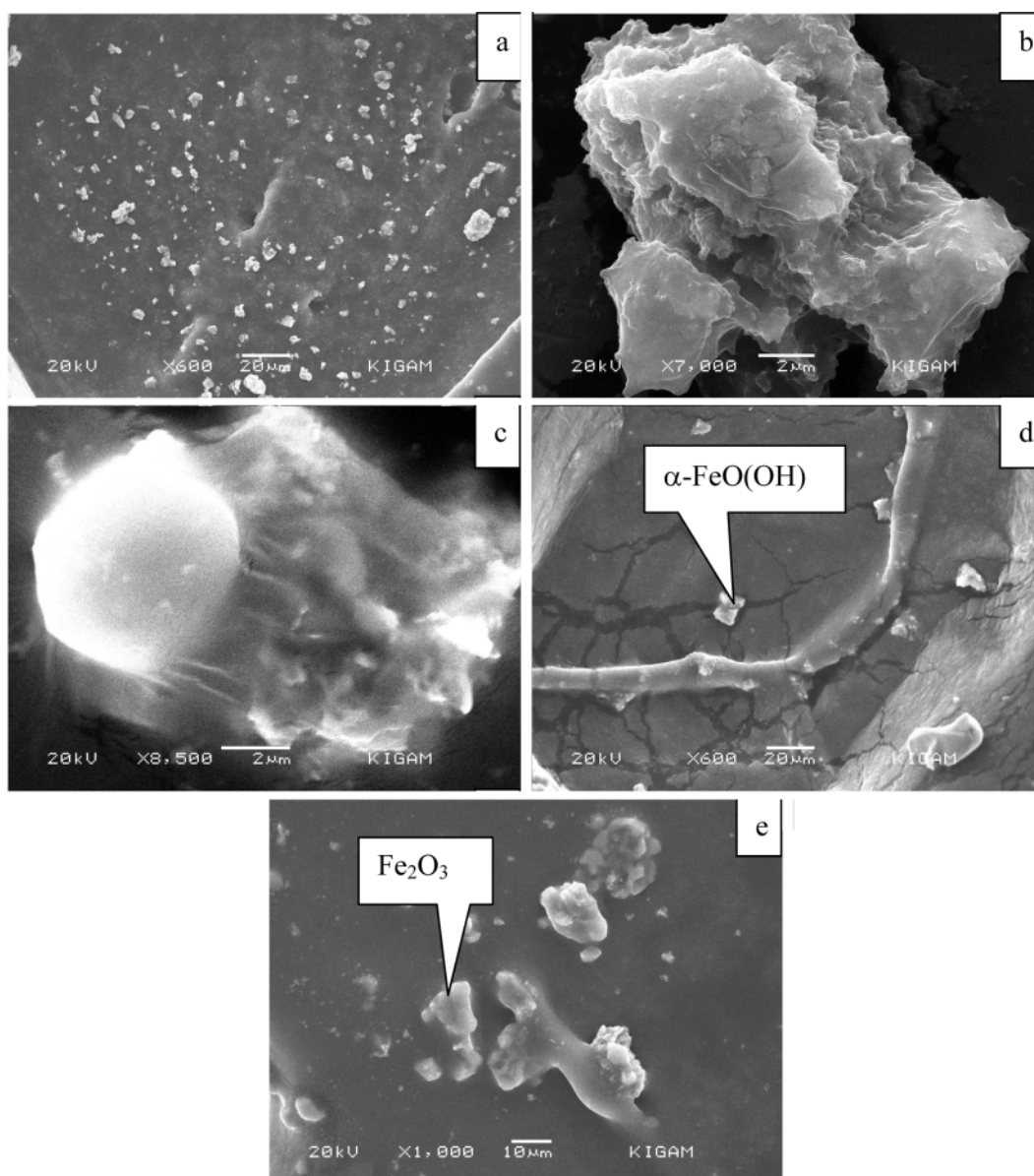

Fig. 4. SEM-micrographs, (a) matte, (b) FeCl₃ leached residue (elemental S coated), (c) FeCl₃+CCl₄ leached residue (elemental S removed), (d) NH₄OH/(NH₄)₂SO₄ leached residue (goethite formation), (e) H₂SO₄ leached residue (hematite formation).

havior, i.e., extraction increased with increasing concentration of HCl. The Ni extraction increased from 12 to 40% and Co extraction increased from 10 to 32%, when HCl concentration was increased from 0.1 to 0.5 M without $FeCl_3$. Whereas, Ni extraction increased from 88 to 95% and Co extraction from 79 to 86% in presence of 1.5 M $FeCl_3$ and similar acid conditions, which indicated that acidity also played a role in Ni and Co extraction. The extraction of Cu, Ni and Co was studied at various temperatures between 30 and 90 °C at a fixed concentration of 1.5 M $FeCl_3$ and 0.3 M HCl. As shown in Table 2, the extraction of all the three metals increased with increase of temperature. The effect was found to be the maximum for Co, followed by Ni and Cu. At 30 °C the reaction was very slow. With increasing temperature from 30 to 90 °C, an acceleration of metal extraction, i.e., 60 to 99.5%, 31 to 93%, and 16 to 85% for Cu, Ni and Co, respectively at 7 h was observed. Based on the results, it was observed that 1.5 M $FeCl_3$, 0.3 M HCl, 90 °C and 7 h appeared to be optimum conditions to extract 99.5% Cu, 93% Ni and 85% Co.

The CCl_4 addition to the reaction mixture in presence of 1.5 M $FeCl_3$ and 0.3 M HCl at various temperatures showed a marked increase in Cu, Ni and Co extraction efficiency. There was no difference in the extraction rate of the metals at the initial stage of the reaction irrespective of temperature. This is understandable, because at the initial stage of the reaction the role of CCl_4 was minimal due to formation of small amount of elemental sulfur. With increasing time, there was marked improvement in the extraction of metals. The effect of CCl_4 was greater at higher temperature compared to lower ones.

The combined application of XRD and SEM studies is a useful tool for the characterization of leached and bulk samples. The samples before and after leaching were subjected to XRD and SEM analysis to see the phase changes and morphological observations. Fig. 1c shows the XRD analysis of matte leached for 7 h using 1.5 M $FeCl_3$ and 0.3 M HCl at 90 °C. As shown in the XRD analysis, $CuFeS_2$ and CuS_2, the two Cu phases present in the matte, dissolved simultaneously in the reaction mixture. The Ni is associated with five different phases, i.e., $(FeNi)_9S_8$, $(FeNi)S_2$, Ni_9S_8, $(CoFeNi)_9S_8$ and Ni_3S_2 in the matte. Out of these, the dissolution of $(FeNi)_9S_8$ appeared to be slow and not complete. The undissolved cobalt was assumed to be the cobalt metal. Although some nickel and cobalt was not leached out (7% Ni and 15% Co), it was not detectable in the XRD analysis. Elemental sulfur was formed with increasing extraction of metals. SEM observations of the leached samples without and with CCl_4 are presented in Fig. 4. Without CCl_4, elemental sulfur can be seen on the leached surface of the residue (Fig. 4b). Whereas, elemental sulfur was not observed in the leached residue when leaching was carried out in the presence of CCl_4 (Fig. 4c). This was supported by the increasing amount of metal extracted into solution in presence of CCl_4. This indicated that metal extraction was hindered by the formation of elemental sulfur, which was subsequently coated around the mineral particles.

2-2. NH_4OH/ $(NH_4)_2SO_4$ Pressure Leaching

The mechanism by which pressure leaching processes affect the release of metals from sulfide mineral matrices, largely dependent on many factors such as temperature, oxygen partial pressure, concentration of leaching reagents, time and process chemistry. The effects of different parameters on the extraction of metals using ammonia/ammonium sulfate pressure leaching process are presented in

Table 3. Effect of different parameters on the extraction of metals using $NH_4OH/(NH_4)_2SO_4$ pressure leaching process

Time, h	$[NH_4OH]$, M	$[(NH_4)_2SO_4]$, M	Oxygen partial pressure, kg/cm^2	Temp., °C	Extraction of Cu, %	Extraction of Ni, %	Extraction of Co, %
0.25	2.0	1.0	15	150	65	73	22
0.50	2.0	1.0	15	150	83	84	37
1.0	2.0	1.0	15	150	91	86	45
2.0	2.0	1.0	15	150	93	88	46
1.0	1.0	1.0	15	150	67	52	17.5
1.0	2.0	1.0	15	150	91	86	45
1.0	3.0	1.0	15	150	92	87	63
1.0	4.0	1.0	15	150	92	87.5	66
1.0	2.0	1.0	15	150	91	86	45
1.0	2.0	2.0	15	150	91.5	81	68
1.0	2.0	3.0	15	150	93	79	71
1.0	2.0	4.0	15	150	94	76	72
1.0	2.0	2.0	5	150	63	38	43
1.0	2.0	2.0	10	150	86	54	58
1.0	2.0	2.0	15	150	91.5	81	68
1.0	2.0	2.0	20	150	94	83	68
1.0	2.0	2.0	25	150	95	84.6	69
1.0	2.0	2.0	15	100	75	62	45
1.0	2.0	2.0	15	125	83	73	61.5
1.0	2.0	2.0	15	150	91.5	81	68
1.0	2.0	2.0	15	175	93	83	72
1.0	2.0	2.0	15	200	94	85	76.5

Table 3. The effects of time show that, all the three metals exhibited similar type of extraction behavior. At the beginning of the leaching, the extraction rate of all the three metals was very fast. Within the first 15 min, 65% Cu, 73% Ni and 22% Co recovery was achieved. This increased to 91%, 86% and 45% for Cu, Ni and Co, respectively, after 1 h leaching time. Beyond 1 h, there was no marked increase in extraction for the studied metals. The variations of NH_4OH concentration at a fixed $(NH_4)_2SO_4$ concentration and vice versa were studied at fixed other conditions. With increasing NH_4OH concentration from 1.0 to 4.0 M and keeping $(NH_4)_2SO_4$ constant at 1.0 M, the extraction of Cu, Ni and Co increased from 67% to 92%, 52% to 87.5% and 17.5% to 66%, respectively, with an equilibrium pH between 8.5 and 9.9. On the other hand, by varying $(NH_4)_2SO_4$ concentration from 1.0 M to 4.0 M and keeping 2.0 M NH_4OH concentration constant, Cu extraction increased marginally from 91 to 94% and Co extraction increased substantially from 45 to 72%, whereas, Ni extraction showed a negative trend. The Ni extraction decreased from 86 to 76% when $(NH_4)_2SO_4$ concentration was increased from 1.0 M to 4.0 M. At the same time, pH also decreased from 9.3 to 8.1. This can be explained by the fact that, at higher pH nickel ammine is the most stable species. In the pH range 6.0-8.0, Ni is precipitated as insoluble nickel hydroxide, thereby decreasing Ni extraction efficiency [23]. The effect of oxygen partial pressure was studied by varying it from 5 to 25 kg/cm², keeping all other parameters such as 2 M NH_4OH, 2 M $(NH_4)_2SO_4$, temperature at 150 °C and time 1 h constant. Extraction of Cu varied from 63 to 95%, Ni varied from 38 to 84.6% and Co from 43 to 69% as oxygen pressure was increased from 5 to 25 kg/cm². For all the three metals, extraction rate was fast up to 15 kg/cm² oxygen partial pressure. With further increase in partial pressure up to 25 kg/cm² the metal extraction was not significantly increased. Similarly, it was found that by increasing the leaching temperature from 100 to 200 °C, Cu extraction increased from 75 to 94%, Ni extraction from 62 to 85% and Co extraction from 45 to 76.5% after 1 h

leaching. So it was concluded that, under the best leaching conditions (2 M NH_4OH+2 M $(NH_4)_2SO_4$, 15 kg/cm² pressure, 200 °C and 1 h), 94% Cu, 85% Ni and 76.5% Co can be effectively recovered.

The leached residue after leaching under best conditions was subjected to XRD analysis to see the phase changes that disappear and/or the products that form during leaching (Fig. 1b). It was observed that, some of the mineral phases like Ni_3S_2, $(FeNi)S_2$, Ni_9S_8, CuS_2 and Co metal completely disappeared within 1 h of leaching. The intensity of $CuFeS_2$ lines decreased with progressive leaching. However, the dissolution of $CuFeS_2$ was incomplete even after 1 h of leaching time. This was presumed to be the contributing factor for the undissolved Cu. The $CuFeS_2$ phase is reported to be the most difficult to leach of all the copper minerals, owing to the formation of a tenacious goethite reaction product under certain conditions [24]. As shown in the XRD, goethite peaks developed as the $CuFeS_2$ phase dissociated. This indicated that the iron present in $CuFeS_2$ was mostly precipitated to goethite and remained in the residue. Similar types of results are also reported by other researchers [25] during ammoniacal leaching of chalcopyrite. The conclusion was further supported by the SEM study shown in Fig. 4. The photograph in Fig. 4a of the matte sample revealed particle aggregates of different initial size without goethite on its surface. After 1 h leaching, goethite was found on the leached surface of the residue, which was subsequently coated around the mineral particles (Fig. 4d). These observations indicated that the goethite formed from the iron was released during dissolution of $CuFeS_2$. On the other hand, whether Ni and Co associated with Fe phases behaves in a similar way or not was not possible to detect in the present study. As shown in the XRD analysis, the undissolved Ni and Co phases were $(FeNi)_9S_8$ and $(CoFeNi)_9S_8$, respectively.

2-3. H_2SO_4 Pressure Leaching

The preliminary experiments showed that temperature, oxygen partial pressure and acid concentration played an important role during H_2SO_4 pressure leaching of matte. The results presented in Table

Table 4. Effect of different parameters on the extraction of metals using H_2SO_4 pressure leaching process

Time, h	[H_2SO_4], % (v/v)	Oxygen partial pressure, kg/cm²	Temp., °C	Extraction of Cu, %	Extraction of Ni, %	Extraction of Co, %	Extraction of Fe, %
0.5	1.0	10	150	96.5	97	97.5	0.8
1.0	1.0	10	150	99.2	99.3	99.5	0.7
1.5	1.0	10	150	99.9	99.9	99.9	0.5
2.0	1.0	10	150	99.9	99.9	99.9	0.3
1.0	0.5	10	150	75.2	95.4	96.8	0.2
1.0	1.0	10	150	99.2	99.3	99.5	0.7
1.0	1.5	10	150	99.6	99.9	99.9	32
1.0	2.0	10	150	99.8	99.9	99.9	45
1.0	1.0	4.0	150	35	89	93	3.2
1.0	1.0	6.0	150	35	89	96	2.9
1.0	1.0	8.0	150	72	98	98	1.6
1.0	1.0	10.0	150	99.2	99.3	99.5	0.7
1.0	1.0	10	110	55	92.5	95	5
1.0	1.0	10	120	59	95.8	96.8	4.4
1.0	1.0	10	130	73	96.7	97.1	3.7
1.0	1.0	10	140	87.5	97.5	97.9	2.6
1.0	1.0	10	150	99.2	99.3	99.5	0.7

4 clearly demonstrate that Cu, Ni and Co extraction was fast and reached equilibrium within 30 min. About 96-97% each of Cu, Ni and Co was extracted within this period. With further increase in time up to 1 h, more than 99% metal extraction was achieved. On the other hand, the Fe concentration in solution decreased with time. For example, within 30 min 0.8% Fe was in the solution; that decreased to 0.3% after 2 h leaching. This can be explained by the precipitation of soluble Fe as hematite with time and remained in the residue. The effect of H_2SO_4 concentration on metal extraction at 10 kg/cm² pressure, 150 °C and 1 h time was studied. It was found that 1.0% (v/v) H_2SO_4 was sufficient enough to extract more than 99% Cu, Ni and Co. With further increasing H_2SO_4 concentration resulted in significant increase in soluble Fe in solution. This is due to the higher acidity in the solution which prevented the precipitation of Fe.

The effects of oxygen partial pressure and temperature were prominent in case of Cu extraction compared to Ni and Co extraction. Cu extraction increased significantly with an increase in oxygen pressure and temperature. For example, Cu extraction increased from 35 to 99.2% and 55 to 99.2% when oxygen partial pressure was increased from 4.0 to 10.0 kg/cm² and temperature from 110 to 150 °C, respectively. Under the same conditions, the variation in Ni and Co extraction was within 10%. Based on the results, it was observed that 1.0% H_2SO_4, 150 °C, 10 kg/cm² and 1h contact time appeared to be optimum to extract 99.2% Cu, 99.3% Ni and 99.5% Co. XRD analysis (Fig. 1d) showed the formation of hematite (Fe_2O_3), which was further confirmed by SEM study (Fig. 4e).

SUMMARY AND COMPARISON AMONG LEACHING PROCESSES

The results of different leaching processes show that they differ considerably in their extraction conditions and efficiency of metal extraction. The merits and disadvantages of a particular process depend on many factors. For example, the availability and cost of fuel, selectivity, extraction efficiency of desired metals, speed of reaction, availability and cost of reagents, reagent consumption, and equipment requirements are among other factors to be considered. A comparison of different leaching processes is presented in Table 5. The extraction of Cu, Ni and Co was more than 99% in case of H_2SO_4

pressure leaching. Whereas, the other two methods suffered by inadequate extraction efficiency of the desired metals (Fig. 3). The leached solution in case of ammoniacal leaching was selective and free from Fe impurities. The leached solution was contaminated with Fe in case of $FeCl_3$ leaching and H_2SO_4 pressure leaching processes which require another processing step to remove Fe. The $FeCl_3$ leaching process results in elemental sulfur as one of the major by-products, a form generally more acceptable environmentally than the SO_4^{2-} from H_2SO_4 pressure leaching and ammoniacal pressure leaching. The time required to achieve maximum extraction efficiency is quite high for $FeCl_3$ leaching (7 h) compared to 1 h for the other two processes. The $FeCl_3$ leaching process is carried out at atmospheric pressure and mild temperature, whereas ammoniacal and H_2SO_4 processes have the disadvantages of operating at high pressure and temperature conditions. The metal extraction efficiency was hindered in case of atmospheric $FeCl_3$ leaching and $NH_3/(NH_4)_2SO_4$ pressure leaching processes due to the formation of elemental sulfur and goethite phases, respectively, which subsequently coated around the mineral particles.

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REFERENCES

1. P. A. Rona, *Science*, **299**, 673 (2003).
2. D. W. Fuerstenau, A. P. Herring and M. Hoover, *Trans. AIME*, **254**, 205 (1973).
3. D. W. Fuerstenau and K. N. Han, *Miner. Process. Technol. Rev.*, **1**, 1 (1983).
4. D. J. Murray, T. W. Healy and D. W. Fuerstenau, *Adv. Chem. Ser.*, **79**, 74 (1968).
5. R. G. Burns and V. M. Burns, *Marine manganese deposits*, G. P. Glasby, Ed., Elsevier, Amsterdam, pp. 185-248 (1977).
6. J. C. Agarwal, N. Becher, D. S. Davis, G. H. Hubred, V. K. Kakaria and R. N. Kust, *J. Met.*, **28**, 24 (1976).
7. P. T. Brooks and D. A. Martin, *Processing of manganiferous sea*

Table 5. Summary of the three different leaching processes

Parameters	$NH_4OH/(NH_4)_2SO_4$ pressure leaching	Atmospheric $FeCl_3$ leaching	H_2SO_4 pressure leaching
Best conditions:			
Leaching reagents	2 M NH_4OH/2 M $(NH_4)_2SO_4$	1.5 M $FeCl_3$/0.3 M HCl	H_2SO_4 (1%), v/v
Time, h	1	7	1
Temperature, °C	200	90	150
Oxygen partial pressure, kg/cm²	15	Atmospheric	10
Extraction of Cu, %	94	99.5	99.2
Extraction of Ni, %	85	93	99.3
Extraction of Co, %	76.5	85	99.5
Role of S	SO_4^{2-}	Elemental S	SO_4^{2-}
Role of Fe	Goethite	Soluble Fe	Hematite
Agitation speed	600	300	600
Pulp density, % (w/v)	5	5	5

nodules, US Bur. Mines, IR 7473 (1971).

8. R. K. Jana, B. D. Pandey and Premchand, *Hydrometallurgy*, **53**, 45 (1999).

9. W. S. Kane and P. H. Cardwell, *Reduction method for separating metal values from ocean floor nodule ore*, U.S. Patent 3,869,360 (1975).

10. W. S. Kane, H. L. McCutchen and P. H. Cardwell, *Recovery of metal values from ocean floor nodules by halidation in molten salt baths*, U.S. Patent 3,894, 927 (1975).

11. S. B. Kanungo and P. K. Jena, *Hydrometallurgy*, **21**, 41 (1988).

12. K. N. Han and D. W. Fuerstenau, *Int. J. Miner. Process.*, **2**, 163 (1975).

13. Y. Zhang, Q. Liu and C. Sun, *Minerals Eng.*, **14**, 525 (2001).

14. R. Acharya, M. K. Ghosh, S. Anand and R. P. Das, *Hydrometallurgy*, **53**, 169 (1999).

15. A. Mukherjee, A. M. Raichur, J. M. Modak and K. A. Natarajan, *Chemical Engineering and Processing*, **44**, 754 (2005).

16. Copper Industry Participants Research Association (Tucson, AZ), "In-Site Mining of Copper Sulphides," March, p. 150 (1991).

17. J. E. Dutrizac, *Can. Metall. Q. (Canada)*, **20**, 307 (1981).

18. C. W. Nam, B. S. Kim and K. H. Park, *The Korean Soc. Geosystem Eng.*, **40**, 191 (2003).

19. C. W. Nam, K. H. Park and H. I. Kim, *The Korean Soc. Geosystem Eng.*, **41**, 413 (2004).

20. K. H. Park, D. Mohapatra and B. R. Reddy, *Separation and Purification Technology*, **51**, 332 (2006).

21. K. H. Park, D. Mohapatra, B. R. Reddy and C. W. Nam, *Hydrometallurgy*, **86**, 164 (2007).

22. T. Deng, *Nickel and cobalt extraction by pressure hydrometallurgy. Proceedings of the international conference on mining and metallurgy of complex nickel ores*, F. Chongyue, H. Huanhua and Z. Chuanfu, Eds., International Academic Publishers, Beijing. PRC, pp. 59-64 (1993).

23. X. Meng and K. N. Han, *Mineral Processing and Extractive Metallurgy Review*, **16**, 23 (1996).

24. K. S. Rao and H. S. Ray, *Minerals Eng.*, **11**, 1011 (1998).

25. K. S. Rao, R. P. Das, P. G. Mukunda and H. S. Ray, *Metallurgical Transactions B*, **24B**, 937 (1993).