

# Nickel and cobalt precipitation from sulphate leach liquor using MgO pulp as neutralizing agent

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## Abstract

The research work presented in this paper determined the conditions at which nickel and cobalt can be recovered, as easily filterable precipitates, from leach liquors, which are produced by sulphuric acid leaching of nickel oxide ores, at atmospheric pressure. More specifically, nickel and cobalt were precipitated as hydroxides at pH = 9, using MgO pulp as a neutralizing agent, by 99.9% and 99.0%, respectively. At this pH value, manganese, which was contained in the leach liquor, was precipitated having a concentration of about 3% in the final mixed precipitate. Statistical design and analysis of experiments were used in order to determine the main effects and interactions of the precipitation factors, which were the pH at equilibrium and the addition of seed material. The characterization of the produced mixed precipitate was carried out by X-ray diffraction, TG-DTA, scanning electron and optical microscopy and particle size distribution analyzer. The main mineralogical phases in the precipitate were theophrastrite (Ni(OH)<sub>2</sub>) and brucite (Mg(OH)<sub>2</sub>). The microscopic observation revealed that the presence of brucite was, mainly, due to the un-reacted MgO pulp, during the precipitation process. This brucite content acted as seed material for nickel precipitation.

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## 1. Introduction

A novel integrated hydrometallurgical method has been developed and patented in order to treat low-grade nickel oxide ores efficiently and economically. It involves heap leaching of the ore by dilute sulphuric acid at ambient temperature, purification of the leach liquors and recovery of nickel and cobalt by solvent extraction and electrowinning (Agatzini and Dimaki, 1991; Agatzini et al., 1999; Tsakiridis and Agatzini, 2004; Agatzini and Karidakis, 2000).

A typical composition of the pregnant solution produced from heap leaching of Greek low-grade nickeliferous laterites with sulphuric acid is the following: Ni<sup>2+</sup> = 5.0 g/l,

Co<sup>2+</sup> = 0.6 g/l, Fe<sup>3+</sup> = 22.0 g/l, Al<sup>3+</sup> = 6.0 g/l, Cr<sup>3+</sup> = 1.0 g/l, Mn<sup>2+</sup> = 0.8 g/l and Mg<sup>2+</sup> = 5 g/l (Agatzini and Dimaki, 2000). After the removal of iron, chromium and aluminum by chemical precipitation (Agatzini et al., 1999), the leach liquor contains nickel, cobalt, magnesium and manganese, which can be separated and recovered by solvent extraction, with suitable solutions for nickel and cobalt electrowinning (Tsakiridis and Agatzini, 2004).

An alternative process for the nickel and cobalt recovery comprises their precipitation as hydroxides. These precipitates can be either further treated in refineries or fed into converters of nickel pyrometallurgical plants.

The present paper presents the results of a research study involving the recovery of nickel and cobalt from purified heap leach liquors by hydrolytic precipitation, using MgO pulp as a neutralizing agent.

Currently, hydrometallurgical processing of laterite ores consists of high-pressure acid leach (HPAL) where the ore

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is leached in  $\text{H}_2\text{SO}_4$  solutions at elevated temperatures and pressures. Following leaching, the solution is preneutralized and prepared for either direct treatment by solvent extraction and subsequent refining of nickel and cobalt or by precipitation to produce an intermediate nickel product (Virnig and MacKenzie, 1999; Jones, 2001; White, 2002). This product (nickel sulphide, nickel carbonate or nickel hydroxide) is further processed prior to sale as a nickel compound or pure metal.

Precipitation is a physical–chemical process, in which soluble metals and inorganics are converted to relatively insoluble metal and inorganic salts (precipitates) by the addition of a precipitating agent. Most often, an alkaline reagent is used to raise the solution pH to lower the solubility of the metallic constituent, and, thus, bring about precipitation. For example, using lime as the precipitating agent to lower the amount of soluble nickel, by forming nickel hydroxide precipitate (“s” denotes solid precipitate) creates the following reaction (Sist and Demopoulos, 2003):



Precipitates, which are small or colloidal, are then coagulated, flocculated, settled, clarified, or filtered out of solution, leaving a lower concentration of metals and inorganics in the effluent. Chemical precipitation depends on several variables, including:

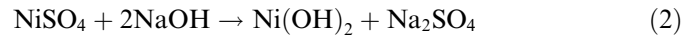
- Maintenance of a proper pH range throughout the precipitation reaction and subsequent settling time.
- Addition of a sufficient excess of treatment ions (precipitating agent) to drive the precipitation reaction to completion.
- Effective removal of precipitated solids.

The precipitation of nickel and cobalt hydroxide by alkali addition is not very selective or without processing difficulties. Therefore, conditions must be optimized to reduce impurity uptake and improve settling characteristics. A number of studies have been performed to determine the conditions of  $\text{Ni}(\text{OH})_2$  precipitation, however the information is limited. According to Sist and Demopoulos, one possible technique used to produce a superior product is controlled supersaturation, which aids in generating well-grown crystalline particles. Precipitates formed via homogeneous nucleation typically possess undesirable properties such as bad morphology (i.e., amorphous or badly formed crystals), slow settling rates, low solids density, and high impurity uptake. Seed must be added to provide a substrate for the precipitation. If supersaturation is badly controlled, the effect of seeding is diminished.

The hydroxides of Ni(II) and Co(II) are known to crystallize in two polymorphic modifications known as  $\alpha$  and  $\beta$  (Rajamathi et al., 2000; Oliva et al., 1982). While the  $\beta$ -form is a stoichiometric phase of the composition  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$ , the  $\alpha$ -form is an anion substituted hydroxyl-deficient phase of the composition  $[\text{Ni}(\text{OH})_{2-x}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}]_n$ ,

where  $\text{A}^{n-} = \text{NO}_3^-, \text{Cl}^-, \text{SO}_4^{2-}, \text{CO}_3^{2-}$ ,  $x = 0.1\text{--}0.2$  and  $y = 0.6\text{--}1.0$ .

According to Tadakazu et al. the precipitation of nickel from sulfate solutions can be represented by the multicomponent ionic reaction:



Nickel hydroxide is precipitated when nickel sulfate and sodium hydroxide react together and the particulate product formed,  $\text{Ni}(\text{OH})_2$ , has an agglomerative nature.

One of the most important factors affecting the precipitation process is the nature of the neutralizing agent. Lime, magnesium hydroxide, caustic, or a blend of these alkaline compounds can be used as a source of hydroxide ions for precipitation of metal hydroxides. Advantages and disadvantages of each of these reagents should be considered in the selection of a system for a particular application. For example, caustic is more expensive than lime, but the cost of chemical feed systems for lime slurry can be substantially more expensive than for caustic. Lime and magnesium hydroxide tend to reduce sludge leachability and break metal complexes that may be present in the wastewater stream (Freeman, 1989).

The nickel and cobalt precipitation reaction involves the creation of a solid precipitate surface from a homogeneous solution, and the initiation of such reactions can be kinetically slow. The presence of nickel/cobalt seed would be expected to eliminate the induction period and to promote the rate of nickel/cobalt precipitation. Consequently, the presence of adequate amounts of the above seed is expected to accelerate the precipitation reaction, produce coarser, more filterable precipitates and suppress undesirable side reactions.

The present research work aimed at the recovery of nickel and cobalt by chemical precipitation, from purified heap leach liquors, using  $\text{MgO}$  as a neutralizing agent. Factorial design of experiments and statistical analysis of the data were used to determine the main effects and interactions of the chosen factors and select the optimum conditions. The factors studied were equilibrium pH and seed addition. The resulting mixed precipitate was investigated by particle size distribution analyzer, X-ray diffraction, TG-DTA, scanning electron microscopy and optical microscopy.

## 2. Experimental

The initial aqueous phase was a pregnant solution, produced from heap leaching of Greek nickel oxide ores with dilute sulphuric acid. The iron, aluminium and chromium content were practically eliminated from the solutions by chemical precipitation at elevated temperature and atmospheric pressure. The solution contained 0.16 g/l of  $\text{Co}^{2+}$ , 3.77 g/l of  $\text{Ni}^{2+}$ , 0.76 g/l of  $\text{Mn}^{2+}$  and 21 g/l of  $\text{Mg}^{2+}$  and its pH was around 4.5.

The precipitation of nickel and cobalt was conducted in 1 l, five-necked, round bottomed split reactors, that were

fitted with a glass stirrer and a pH electrode. Seed material was added before neutralization and it had been produced from a real leach solution by neutralization with MgO (industrial grade) to a pH value of 8.5, at ambient temperature. Chemical analysis of the seed is shown in Table 1.

The pH of the solution was measured using a METTLER 465-50-T-S7 combined pH electrode, specially designed for semi-solid solutions. The pH was slowly raised to a pre-determined equilibrium value, by adding the neutralizing agent. It should be emphasized that, during the precipitation process, the pH increase rate was kept low in order to control supersaturation of nickel and cobalt and avoid the production of an amorphous precipitate. At the end of the runs, the content of the reactor was filtered under vacuum. The resulting precipitates were washed with water by re-pulping, dried overnight at 110 °C and weighed.

The precipitate obtained as described above was analyzed chemically as well as mineralogically by X-ray diffraction (XRD), using a Siemens D5000 diffractometer with nickel-filtered Cu K $\alpha_1$  radiation (= 1.5405 Å), 40 kV and 30 mA.

TG/DTA analysis was conducted with a Setaram–Lab-sys thermal analyzer. Type S-thermocouple is used for tem-

perature measurements in this instrument. The sample was placed in a ceramic crucible and heated from room temperature to 700 °C at a heating rate of 5 °C/min using air as a medium under static condition. TG/DTA were done simultaneously.

The morphology of the precipitate was also examined by scanning electron microscopy (SEM) using a Jeol 6100 scanning electron microscope. Experimental conditions involved 10 kV accelerating voltage.

Optical microscopy was performed in thin sections. Thin sections were produced by vacuum impregnation, of the selected sample, with epoxy resin, followed by cutting, grinding, and polishing, until a final thickness of 20  $\mu$ m is reached. During the process the thin section was mounted upon an object glass. The microscopic observation of the thin sections was achieved using a Karl Zeiss–Jenapole optical microscope in transmitted light.

Finally, the particle size distribution of the produced precipitate was measured by a Cilas-Model 1064 laser scattering particle size distribution analyzer. An amount of 0.1 g of sample powder was put in 100 ml of ethanol and underwent dispersion treatment by an ultrasonic dispersion unit for 60 s.

### 3. Results and discussion

#### 3.1. Effect of pH on the nickel, cobalt and manganese precipitation

Preliminary runs were conducted, using a synthetic solution, to draw the precipitation curves of nickel and cobalt as a function of pH, by the addition of MgO pulp (20%) as neutralizing agent. The solution contained 4.5 g/l Ni,

Table 1  
Chemical analysis of the seed material used

Element	Content (%)
Ni	28.52 $\pm$ 0.56
Co	1.64 $\pm$ 0.04
Mn	2.50 $\pm$ 0.1
Mg	16.85 $\pm$ 2.08

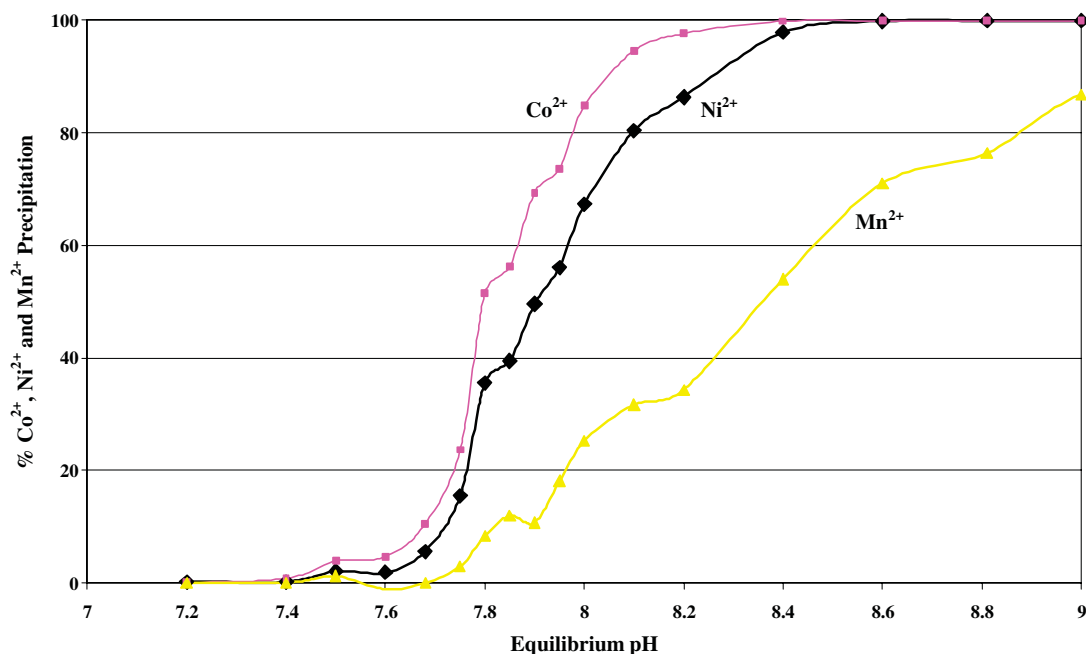


Fig. 1. Nickel, cobalt and manganese precipitation using MgO pulp as neutralizing agent.

0.25 g/l Co and 0.84 g/l Mn. Samples were taken at specific pH values, they were filtered and the solutions were analyzed. The results, presented in Fig. 1, show that complete precipitation of nickel and cobalt takes place at a pH range of 8.2–8.8, while manganese precipitation reached 85%. In this pH range magnesium precipitation did not exceed 20%.

### 3.2. Statistical study of the precipitation process

Factorial design and analysis of experiments were used in order to determine the main effects and interactions of the precipitation factors (Box et al., 1978). The factors studied and their levels for nickel and cobalt precipitation are shown in Table 2. Parameters, which were kept constant during experimentation, were:

- stirring speed = 1200 rpm
- initial cobalt concentration = 0.16 g/l
- initial nickel concentration = 3.77 g/l
- initial manganese concentration = 0.76 g/l
- initial magnesium concentration = 21.0 g/l
- temperature = 25 °C
- neutralizing agent = 20% MgO (industrial grade) pulp

Table 2  
Nickel and cobalt precipitation

Factor	Variables	Low	High	Units measured
		level (-)	level (+)	
<i>A</i>	Equilibrium pH (pH)	8.2	9.0	pH units
<i>B</i>	Seed addition (S)	0.0	20.0	g/l

Minimum and maximum levels of variables.

Table 3  
% Metals precipitation from sulphate solution by 20% MgO pulp as a neutralizing agent

Treatment code	Variables studied		Nickel (%)	Cobalt (%)	Manganese (%)	Reaction time (min)
	<i>A</i> (pH)	<i>B</i> (seed)				
<i>I</i> <sub>1</sub>	–	–	52.05	85.66	42.05	320
<i>I</i> <sub>2</sub>	–	–	58.62	89.85	43.04	335
<i>α</i> <sub>1</sub>	+	–	99.93	99.04	89.07	370
<i>α</i> <sub>2</sub>	+	–	96.34	99.30	89.90	360
<i>b</i> <sub>1</sub>	–	+	73.62	95.70	37.41	235
<i>b</i> <sub>2</sub>	–	+	74.62	97.20	38.41	230
( <i>αb</i> ) <sub>1</sub>	+	+	99.93	99.04	92.21	330
( <i>αb</i> ) <sub>2</sub>	+	+	99.87	98.50	84.76	320

Table 4  
Chemical analyses of the produced mixed precipitate

Treatment code	Variables studied		Nickel (%)	Cobalt (%)	Manganese (%)	Magnesium (%)
	<i>A</i> (pH)	<i>B</i> (seed)				
(1)	–	–	33.52 ± 0.56	2.90 ± 0.04	1.25 ± 0.1	22.84 ± 2.08
<i>a</i>	+	–	18.42 ± 0.56	1.12 ± 0.04	3.20 ± 0.1	27.06 ± 2.08
<i>b</i>	–	+	29.58 ± 0.56	1.84 ± 0.04	2.41 ± 0.1	17.72 ± 2.08
<i>ab</i>	+	+	24.96 ± 0.56	1.43 ± 0.04	3.24 ± 0.1	26.00 ± 2.08

The main responses under investigation were the percentages of cobalt and nickel precipitation. The precipitation percentages of cobalt, nickel and manganese, as well as the reaction times are given in Table 3.

As can be seen in Table 3, nickel precipitation varied from 55% to 100%, whereas cobalt precipitation was higher and ranged from 87% to 99%. Under the present experimental conditions magnesium precipitation reached 20%, whereas manganese precipitation was also high and varied from 43% to 88%. However, the manganese level in the mixed precipitate, compared to nickel was very low, as it is shown in Table 4. The magnesium presence in the mixed precipitate was mainly attributed to the un-reacted MgO pulp, which remains in the solution, as it was shown from the mineralogical study of the precipitate.

To study the main effects and interactions of the factors on the nickel and cobalt precipitation, a Yates' analysis and an analysis of variance were carried out on the percentages of Ni<sup>2+</sup> and Co<sup>2+</sup> precipitation from sulphate solutions in the presence of Mn<sup>2+</sup> and Mg<sup>2+</sup>. The results are shown in Tables 5 and 6, respectively.

Regarding nickel precipitation, the main effects *A* (equilibrium pH) and *B* (seed addition) were found to be statistically significant at  $\alpha = 0.01$  and positive (Table 5). In the range of variables studied, the interaction of the two factors (*AB*) was found to be statistically non significant, a fact that indicates that the factors *A* and *B* act independently from each other and positively on the response. As a result, the high value of pH (9.0) and the addition of seed in the reactor maximize nickel precipitation.

Regarding cobalt precipitation (Table 6), only the main effect *A* (equilibrium pH) was statistically significant at  $\alpha = 0.01$  and positive, meaning that this variable operates

Table 5  
Yates' analysis and analysis of variance

Treatment code	Response Ni <sup>2+</sup> precipitation (%)	Yates' analysis					Analysis of variance			
		1	2	Divisor	Effects	Identification	$t = \text{eff}/s_e$	$t_{0.01} \Phi = 4$	Significance at $\alpha = 0.01$	
(1)	55.31 ± 1.9	155.24	330.78	4	82.70 ± 0.95	Average				
<i>a</i>	98.14 ± 1.9	175.54	68.88	2	34.44 ± 1.9	<i>A</i>	18.06	4.6	S	
<i>b</i>	74.12 ± 1.9	44.62	20.3	2	10.15 ± 1.9	<i>B</i>	5.41	4.6	S	
<i>ab</i>	99.90 ± 1.9	24.26	-20.36	2	-10.18 ± 1.9	<i>AB</i>	-4.49	4.6	NS	

Response: Percentage of Ni<sup>2+</sup> precipitation from sulphate solution.

Table 6  
Yates' analysis and analysis of variance

Treatment code	Response Co <sup>2+</sup> precipitation (%)	Yates' analysis					Analysis of variance			
		1	2	Divisor	Effects	Identification	$t = \text{eff}/s_e$	$t_{0.01} \Phi = 4$	Significance at $\alpha = 0.01$	
(1)	87.76 ± 1.12	186.3	381.44	4	95.36 ± 0.56	Average				
<i>a</i>	99.17 ± 1.12	195.14	14.64	2	7.32 ± 1.12	<i>A</i>	6.64	4.6	S	
<i>b</i>	96.45 ± 1.12	11.78	8.84	2	4.42 ± 1.12	<i>B</i>	3.95	4.6	NS	
<i>ab</i>	98.77 ± 1.12	2.86	-8.92	2	-4.46 ± 1.12	<i>AB</i>	-3.98	4.6	NS	

Response: Percentage of Co<sup>2+</sup> precipitation from sulphate solution.

independently. The non significance of the seed addition in the precipitation of cobalt, in contrast to nickel precipitation, can be attributed to the fact that the nickel precipitates act as seed material for cobalt precipitation. The presence of seed material would probably be beneficial for the precipitation of cobalt from a solution without the simultaneous precipitation of another metal.

Based on the statistical analysis of the results, the optimum conditions determined for the simultaneous nickel and cobalt precipitation from sulphate solution are: equilibrium pH = 9.0, seed addition = 20 g/l.

### 3.3. Characterization of the precipitate

The particle size distribution of the produced precipitate is given in Fig. 2. It was found that 50% of the mixed precipitate was below 14 µm, whereas 100% of the material was below 95 µm. The mean diameter of the precipitate was computed at 11.8 µm.

The X-ray diffraction data of the produced precipitate, using MgO pulp as neutralizing agent, shown in Fig. 3. The main mineralogical phases are theophrastrite (Ni(OH)<sub>2</sub>) and brucite (Mg(OH)<sub>2</sub>). The main peaks, which correspond

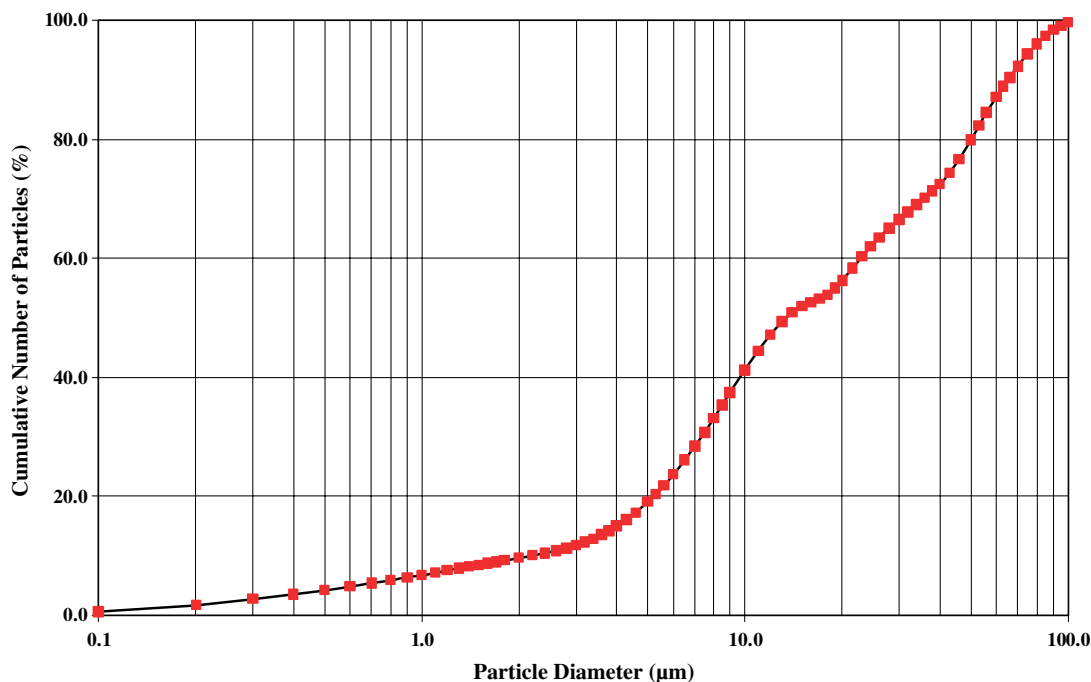


Fig. 2. Particle size distribution of the produced mixed precipitate by laser scattering analyzer.

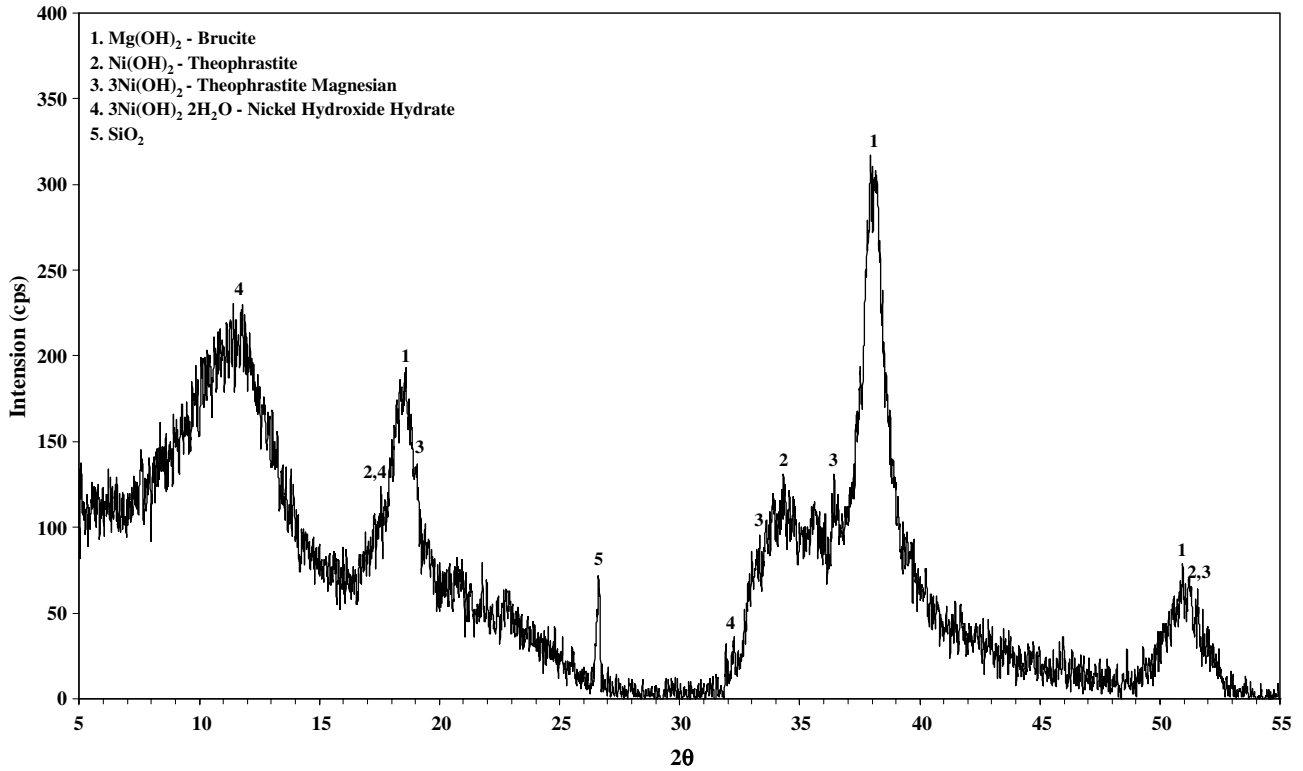


Fig. 3. Mineralogical phases of the produced mixed precipitate using MgO pulp as neutralizing agent.

to  $Mg(OH)_2$ , were sharper and with higher intensity, compared with those of  $Ni(OH)_2$ , whose peaks displayed lower intensity and higher peak width. The above differences were attributed to the differences in the degree of crystallin-

ity of the two main products. More specifically, the main peaks of  $Ni(OH)_2$  characterize a fine crystallized material with no well-developed crystals, whereas the main peaks of  $Mg(OH)_2$  reveal a better-crystallized compound. The

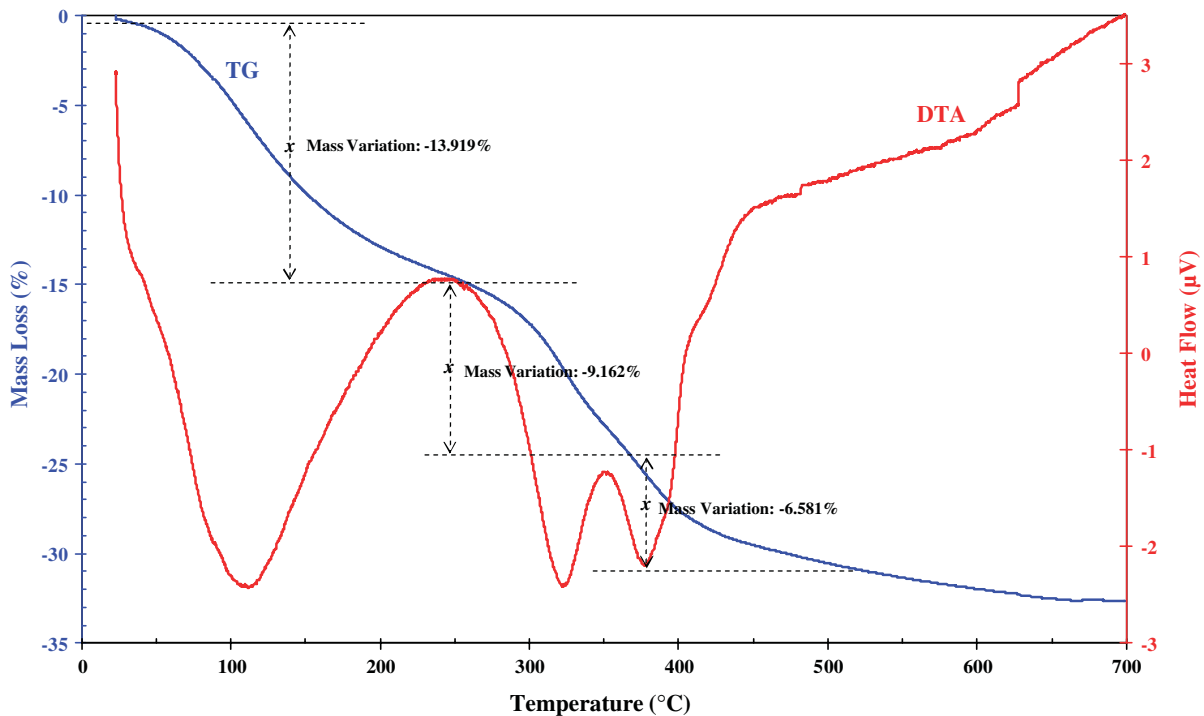
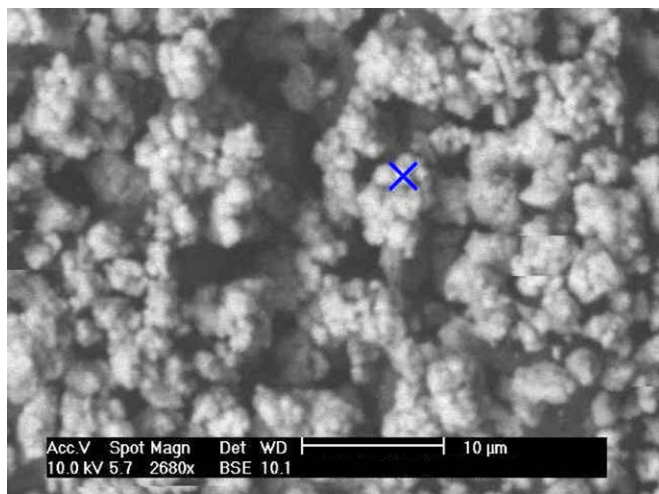
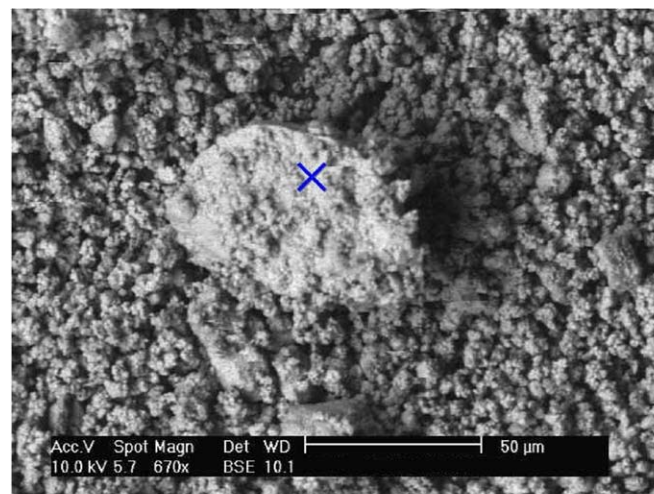


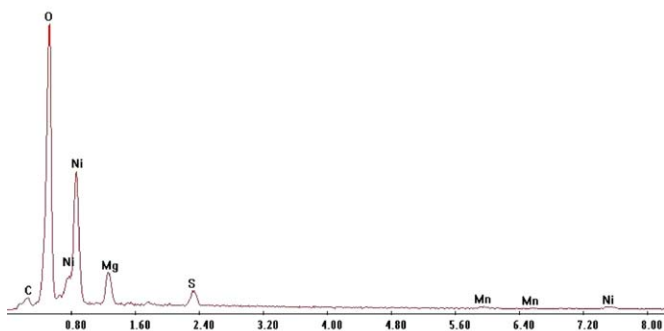
Fig. 4. TG and DTA analysis of the produced mixed precipitate.



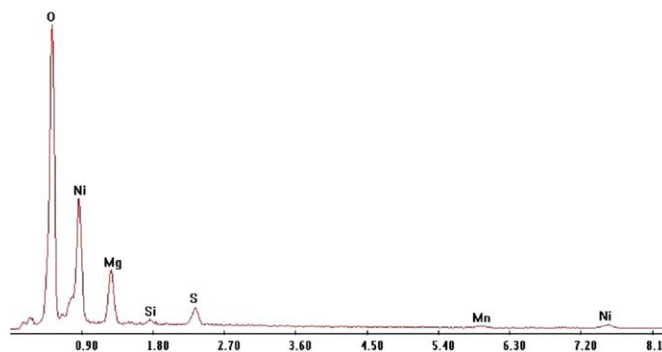
(a)



(a)



(b)



(b)

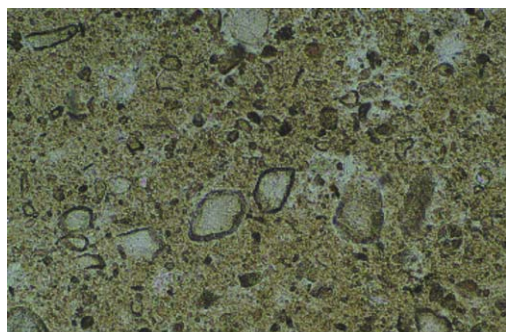
Fig. 5. SEM micrographs of the produced mixed precipitate. (a) Fine agglomerates of  $\text{Ni}(\text{OH})_2$  crystals. (b) Composition of the above marked spot.

Fig. 6. SEM micrographs of the produced mixed precipitate. (a) Formation of fine  $\text{Ni}(\text{OH})_2$  crystals on the surface of  $\text{Mg}(\text{OH})_2$  course crystal. (b) Composition of the above marked spot.

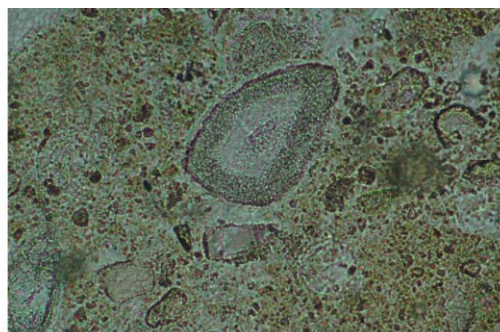
detection of small quantities of  $\text{SiO}_2$  was attributed to its presence in the neutralizing agent. Mineralogical phases of cobalt and manganese were not detected, probably because of their low content in the mixed precipitate.

From the study of Fig. 4 (TG and DTA) of the above mixed precipitate the weight loss up to  $110^\circ\text{C}$  can be attributed to the removal of humid water, while the weight loss ( $\sim 9\% + 6.5\%$ ) up to  $400^\circ\text{C}$  and the heat absorbance

(endothermic peaks at  $320^\circ\text{C}$  and  $380^\circ\text{C}$ ) can be attributed to the dehydroxylation reaction of hydroxides and the water removal from the  $\text{Ni}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ , according to the reactions (Mackenzie, 1972):



(a)



(b)

Fig. 7. Microstructure of the produced mixed precipitate in thin sections. (a) Brucite crystals in fine  $\text{Ni}(\text{OH})_2$  matrix ( $\parallel$ ,  $\times 100$ ). (b) Course  $\text{Mg}(\text{OH})_2$  crystal which has acted as seed material for  $\text{Ni}(\text{OH})_2$  precipitation ( $\parallel$ ,  $\times 200$ ).

The results of the mineralogical analysis by X-ray diffraction were also confirmed by electron microscopic observations. Nickel hydroxides were detected with the form of fine aggregates, whereas magnesium hydroxide with the form of large crystals. As shown in Fig. 5, nickel hydroxide precipitate was in the form of aggregates of fine crystallites. The aggregates had an irregular shape and a homogeneous size of about 5  $\mu\text{m}$  (longest dimension). On the other hand, magnesium hydroxide mainly consisted of large crystals with size from 50 to 90  $\mu\text{m}$  (Fig. 6). Furthermore, nickel hydroxide aggregates were formed on the surface of magnesium hydroxide crystals. These observations were also confirmed and from the optical microscopy in thin sections in transmitted light. As shown in Fig. 7 nickel hydroxide has been formed around the magnesium hydroxide crystal in a depth of 40  $\mu\text{m}$ . This fact led to the conclusions that the magnesium hydroxide presence in the mixed precipitate was, mainly, due to the unreacted pulp, during the precipitation process, which acted as a seed material for nickel precipitation.

#### 4. Conclusions

The present experimental work has shown that nickel and cobalt can be quantitatively precipitated, at ambient temperature, as an easily filterable material.

The precipitation of nickel and cobalt by 99.9% and 99%, correspondingly, was accomplished by gradually raising the initial pH of the leach liquor to a value of 9.0, at such a rate as to keep supersaturation of nickel and cobalt as low as possible, within a practical period of time. At those conditions, manganese precipitation reached 80%.

The addition of seed material had a positive effect on the efficiency of precipitation.

The composition of the mixed precipitate at the optimum conditions of precipitation was 25% Ni, 1.5% Co, 3% Mn and 26% Mg.

The main mineralogical phases of the mixed precipitate were  $\text{Ni}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . Nickel hydroxide was in the form of aggregates of fine crystallites. The aggregates had an irregular shape and a homogeneous size of about 5  $\mu\text{m}$ . Magnesium hydroxide consisted of large crystals with size in the range 50–90  $\mu\text{m}$ . Nickel hydroxide was

observed to have also been formed around the magnesium hydroxide crystals, forming a layer of 40  $\mu\text{m}$  thick. This fact led to the conclusion that the presence of magnesium hydroxide in the mixed precipitate was, mainly, due to the unreacted magnesium hydroxide, which acted as seed material for nickel precipitation.

#### References

- Agatzini, S., Dimaki, D., 1991. Recovery of nickel and cobalt from low-grade nickel oxide ores by heap leaching with dilute sulphuric acid at room temperature, Greek patent no. 1001555.
- Agatzini, S., Dimaki, D., 2000. Method for extraction of nickel and/or cobalt from nickel and/or cobalt oxide ores by heap leaching with a dilute sulphuric acid solution, prepared from sea water, at ambient temperature, Greek patent no. 1003569.
- Agatzini, S., Karidakis, T., 2000. Production of a magnesium hydroxide—containing mixture suitable for use as a filler in polymers and as an additive in cement, Greek patent no. 1003693.
- Agatzini, S., Oustadakis, P., Zafeiratos G., 1999. Removal of aluminum and chromium from nickel–cobalt sulphate solutions, Greek patent no. 1003419.
- Box, G.E.P., Hunter, W.G., Hunter, J.S. (Eds.), 1978. Statistics for experiments. John Wiley, New York.
- Freeman, H.M. (Ed.), 1989. Standard Handbook of Hazardous Waste Treatment and Disposal. McGraw-Hill, New York.
- Jones, D.L., 2001. Process for extraction of metal from an ore or concentrate containing nickel and/or cobalt. US patent no. 6171564.
- Mackenzie, R., 1972. Differential Thermal Analysis, Vol. 2. Academic Press.
- Oliva, P., Leonardi, J., Laurent, J.F., Delmas, C., Braconnier, J.J., Figlarz, M., Fievet, F., de Guibert, A., 1982. Review of the structure and the electrochemistry of nickel hydroxides and oxy-hydroxides. *J. Power Sources* 8 (2), 229–255.
- Rajamathi, M., Kamath, P.V., Seshadri, R., 2000. Chemical synthesis of  $\alpha$ -cobalt hydroxide. *Mater. Res. Bull.* 35 (2), 271–278.
- Sist, C., Demopoulos, G.P., 2003. Nickel hydroxide precipitation from aqueous sulfate media. *JOM* 55 (8).
- Tadakazu, I., Hideki, T., Ayumu, F., Mikiko, F., 1999. Reactive crystallization of nickel hydroxide particles in continuous reactive crystallizer. In: Garside, J. (Ed.), Proc. 14th Int. Symp. Industrial Crystallization. IChemE, Cambridge, UK.
- Tsakiridis, P.E., Agatzini, S.L., 2004. Simultaneous solvent extraction of cobalt and nickel in the presence of manganese and magnesium from sulfate solutions by Cyanex 301. *Hydrometallurgy* 72, 269–278.
- Virnig, M.J., MacKenzie, M., 1999. Process for the recovery of nickel. US patent no. 5976218.
- White, D.T., 2002. Selective precipitation of nickel and cobalt. US patent no. 6409979.