

Article

Microwave and Ultrasound Effect on Ammoniacal Leaching of Deep-Sea Nodules

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Received: 19 July 2018; Accepted: 9 August 2018; Published: 14 August 2018



Abstract: The influence of ultrasound and microwaves on extraction of copper, nickel, and cobalt from manganese deep-sea nodules by reductive ammoniacal leaching in the presence of ammonium thiosulfate as a reducing agent was studied. The ultrasonic ammoniacal leaching provides higher metals extraction, while the effect of microwaves on the metals extraction under the studied leaching conditions is insignificant. In general, increasing leaching temperature increases significantly extraction of the metals of interest. At high temperatures, extraction efficiencies of copper, nickel, and cobalt decrease over longer leaching duration as a result of decomposition of the metals amino-complexes and reverse precipitation of metals. However, during the ultrasonic leaching at a temperature of 85 °C, the extraction of nickel remains almost unchanged over longer leaching durations and does not follow the decreasing course, observed in the extraction of copper and cobalt. The finding suggests that nickel can be selectively extracted from the nodules by the ultrasonic leaching. The maximal extraction efficiency of copper, nickel, and cobalt was 83%, 71%, and 32%, respectively, when the reductive ultrasonic ammoniacal leaching was carried out at 85 °C for 90 min. In the presence of microwaves, the maximal extraction efficiency of copper, nickel, and cobalt was 67%, 48%, and 8%, respectively, when the reductive ultrasonic ammoniacal leaching was carried out at the output power of 60 W for 210 min.

Keywords: deep-sea nodules; ammoniacal leaching; ultrasound; microwaves

1. Introduction

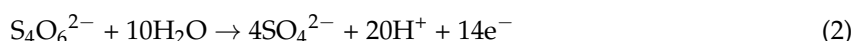
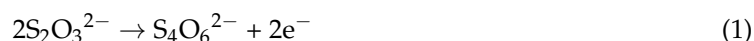
Polymetallic deep-sea nodules are a promising raw material for recovering non-ferrous metals, especially copper, nickel, cobalt, and manganese. Beside a relatively high amount of iron, they also contain in trace amounts important metals, such as rare earth elements (REEs), Li, Mo, and so on. The highest occurrence of nodules is in the Clarion and Clipperton fracture zones in the North Pacific between Hawaii and Mexico [1–4]. The nodules are ovate or spherical black-colored segments enclosed in sediments, large in size from 1 to 25 cm (approximately 5 cm in diameter). The metal coatings around the nodule core have a concentric layered, radially dendritic, massive, or combined macrostructure. Two different zones are inside the casing, the dendritic zone is a result of the diagenetic mobilization of the metals from the sediment, and the concentric zone is formed by the precipitation of hydroxides from the seawater [3]. Nodules are made of a mixture of oxides (manganese oxides, goethite, and opal), clay minerals, and a small number of other minerals—apatite, barite, celestite, and so on. The composition of manganese minerals varies according to the depth of occurrence; birnessite occurred until the depth of 3000 m, with todorokite and vernadite occurring deeper. Manganese nodules contain 12.29–33.98% of manganese, 1.62–15.75% of iron, 0.097–1.080% of nickel, 0.0075–0.0358% of cobalt, and 0.061–0.711% of copper. They also contain lead, barium, molybdenum, titanium, zinc, vanadium, chromium, lithium, and zirconium [2]. The utilization of nodules,

except for the extraction of non-ferrous metals, could in the future be for industrial gas purification, dehydrogenation of hydrocarbons, and adsorption of heavy metals from aqueous solutions or as complex mineral fertilizers [2,3].

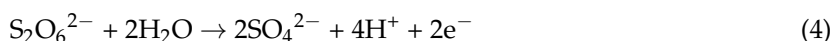
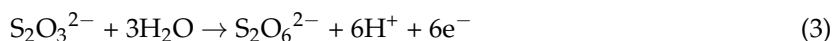
Nowadays, two categories of extraction processes are used to obtain the metals of interest selectively or collectively; pyrometallurgical pretreatment followed by hydrometallurgical treatment, and solely hydrometallurgical treatment—leaching. Melting, reductive roasting, sulfation, or chlorination are used as pyrometallurgical pretreatment for copper, nickel, and cobalt. These nonferrous metals are then converted into the soluble ammine complexes during ammoniacal leaching, but iron and manganese remain undissolved [5–8]. Separate leaching is performed in hydrochloric acid; sulfuric acid; ammonia; or in the presence of a reducing agent, for example, sulfur dioxide, pyrite, sodium sulfide, iron(II) sulfate, or ethanol [9–11].

It has been found that reduction of MnO_2 from the nodules is an important step to reach good leaching efficiency for copper, nickel, and cobalt [12,13]. In this work, ammonium thiosulfate $((\text{NH}_4)_2\text{S}_2\text{O}_3)$ was used as the reducing agent. Thiosulfate can be easily oxidized into tetrathionate $(\text{S}_4\text{O}_6^{2-})$, elemental sulfur (S), dithionate $(\text{S}_2\text{O}_6^{2-})$, and sulfate (SO_4^{2-}) , depending on the redox potential of the oxidizing agent. The oxidation potential of the MnO_2/MnO system is thermodynamically preferable for the oxidation of thiosulfate $(\text{S}_2\text{O}_3^{2-})$ to sulfate (SO_4^{2-}) via dithionate $(\text{S}_2\text{O}_6^{2-})$ as an intermediate. However, depending on the conditions, dithionate $(\text{S}_2\text{O}_6^{2-})$ can be kinetically stable and does not oxidize to sulfate at lower temperature and pH [14].

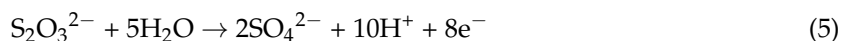
Oxidation of thiosulfate to sulfate via tetrathionate as an intermediate can occur as follows:



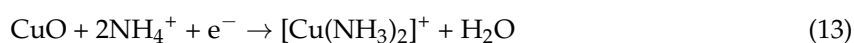
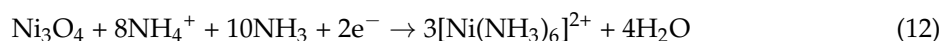
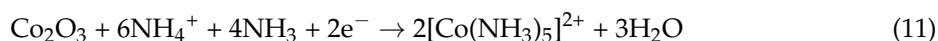
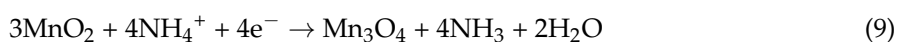
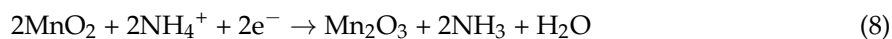
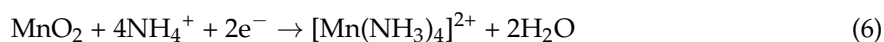
Oxidation of thiosulfate to sulfate via dithionate as an intermediate can occur as follows:



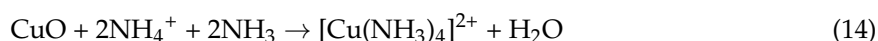
The overall reaction is given by combining the reaction (3) and the reaction (4):

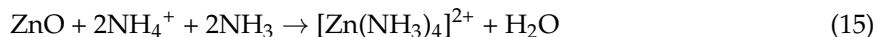


Reductive dissolution of metal oxides from nodules can occur as follows:

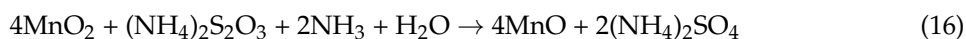


Dissolution of metal oxides from concretions can also occur without changing the oxidation state:





Reductive dissolution of CuO (Equation (13)) is faster than the non-reductive one (Equation (14)). Cu^+ , Mn^{2+} , and Fe^{2+} ions, which are formed during leaching or added into the solution before leaching, catalyze the leaching process. Soluble manganese and iron ammine complexes $[\text{Mn}(\text{NH}_3)_4]^{2+}$ and $[\text{Fe}(\text{NH}_3)_4]^{2+}$ are soluble when the pH is between 9.2 and 9.8. Ammonium thiosulfate is added mainly because of the reduction of MnO_2 to MnO . The amount of ammonium thiosulfate added is in the range of 0.5 to 2 (optimally 1.5) times the stoichiometric amount calculated according to the summary Equation (16) = Equation (5) + Equation (7):



Ultrasound has good potential in the pretreatment of solid samples and speeds up operations such as extraction of organic and inorganic compounds [15], dispersion of suspensions [16–18], homogenization [19], spraying [20], and elutriation [21]. Ultrasonically assisted leaching is an effective way to extract a large number of analytes from different sample types. High extraction is a result of very high temperatures and pressures produced by ultrasonication at the interface between an aqueous or organic solution and solid phase, in combination with the oxidative energy of the radicals formed during the sonolysis, for example, hydroxyl and hydrogen peroxide in the case of water sonolysis. High temperatures increase solubility and diffusivity, and high pressures facilitate the penetration and transport [22]. The main advantages of continuous ultrasonic assisted leaching are a lower sample and agent consumption, an overall smaller amount of chemicals required for dissolution, compared with the conventional method. In the solid–liquid system, the presence of high-frequency ultrasonic waves leads to the formation of expansion and compression cycles, and consequently, the cavitation bubbles are formed. The breakdown of these bubbles creates local high-speed micro-currents that lead to erosion and cracking at the surface of the solid. This phenomenon allows better penetration of the liquid into the solid and the target metals are more easily dissolved [23]. The reported experiments demonstrated higher yields and faster dissolution, and hence improved metal extraction from solid samples when sonication was used. The results show that ultrasound can be a vital method for metal extraction in the future, to minimize energy consumption and optimize control over chemical reactions [24].

Another environmentally friendly technique for extracting metals from solid samples is microwave-assisted leaching. Extraction by microwaves has several advantages in comparison with conventional methods, such as better controllable and selective heating, and faster processing because microwave radiation, typically between 915 MHz and 2.54 GHz, delivers energy to where it is needed. Numerous studies on the leaching of copper from chalcopyrite by microwave energy, as well as gold leaching from ores, have been reported by Al-Harashsheh and Kingman [25]. Typically, these studies have shown increased metal extraction. Xia, Pickles, and Wu et al. have concluded that metal extraction from industrial residues, assisted by microwaves, significantly reduces the time required for extraction [18,26]. Microwaves have advantages for leaching in comparison with ultrasound [27,28]. Ultrasonic devices are usually less stable as a result of the aging of the ultrasonic probe surface. This leads to decrease in the extraction efficiency. In microwave-assisted leaching, the particle size is not a critical factor in comparison with ultrasound-assisted applications.

The goal of this work was to verify the possibility of using ultrasound and microwaves in ammoniacal leaching of deep-sea nodules by ammonium thiosulfate and to determine the optimal conditions for recovering copper, nickel, and cobalt from the nodules.

2. Materials and Methods

The deep-sea nodules were provided by Interoceanmetal Joint Organization, Szczecin, Poland. The nodules were ground in a ball mill for 10 min and the milling product was sieved. For each experiment, 25 g of nodules with particles size under 250 μm was added into 250 mL of solution (solid to liquid ratio 1:10). The content of the main metals in the studied nodules is shown in Table 1.

Table 1. Content of main metals in nodules.

Element	Mn	Fe	Cu	Ni	Co	Zn
wt %	30.57	4.41	1.18	1.14	0.13	0.14
Element	Al	Si	Mg	Ca	Na	Ti
wt %	2.16	3.53	1.87	1.84	1.64	0.35

The nodules were added to the solution containing 65.5 mL of ammonia (25 wt % solution, density 908 g/dm³) and 184.5 mL of distilled water. The suspension was mixed with a magnetic stirrer in a 300 mL reaction vessel with a lid, into which a speed-controlled stirrer, a spiral water cooler, and a mercury thermometer were implemented. The ammonium sulfate was added in such a way that the pH of the resulting solution was adjusted to 10. Subsequently, the mixture was kept at room temperature or heated to 50 °C or 85 °C, using a thermostatic bath. The amount of ammonium thiosulfate calculated from Equation (16), 7.6 g, was used. Ammonium thiosulfate solution was heated separately on a magnetic stirrer and added to the mixture over 2 min at the selected temperature. In the case of ammoniacal leaching assisted by ultrasound, an air-cooled ultrasonic titanium probe was inserted into the reactor. The probe was connected to an ultrasonic generator with the output power of 100 W, with operating frequency of 28 kHz. During ammoniacal leaching assisted by microwave, the reaction vessel was wrapped in aluminium foil and placed in a protective metal net. The microwave assisted leaching was carried out in the protected reaction vessel, into which a glass protected microwave probe was inserted. Microwaves were generated by a microwave generator with the output power of 300 W. The microwave intensity was set for the first leaching at 30 W and for the second one at 60 W. The temperature inside the reaction vessel was measured by a laboratory thermometer. Microwave safety has been controlled using the Voltcraft MT-128 sensor (Comrad-Electric Ltd., Colchester, UK). In the last experiment, ultrasound and microwaves were used together. During leaching experiments, 10–20 mL of leaching solutions were taken out at chosen time intervals and filtered off. At the end of the leaching test, the remaining solution was filtered off and washed with 100 mL of distilled water. Leaching residues were dried off at 50 °C and submitted to X-ray analysis. Metals concentrations in solutions were analysed by the atomic absorption spectrometer GBC 932plus (GBC Scientific Equipment Ltd., Dandenong, Australia). The pH was measured by pH meter Orion 525 (ThermoFisher Scientific™, Grand Island, NY, USA), equipped with a glass electrode Hamilton Liq-Glass (Hamilton, Reno, NV, USA).

3. Results

3.1. Ammoniacal Leaching

The results of ammoniacal leaching at room temperature indicate that the amount of metals extracted into the solution was minimal (Table 2, Figure 1). After four hours of leaching, only 28 mg/L of copper, 2 mg/L of nickel, and 0.3 mg/L of cobalt were detected in the leaching liquors, corresponding to the extraction efficiencies of 2.38% of Cu, 0.18% of Ni, and 0.23% of Co.

Table 2. Metals concentration and extraction efficiency of ammoniacal leaching at room temperature.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	11.4	0.6	0.2	0.97	0.05	0.15	9.99
10	11.5	0.6	0.2	0.97	0.05	0.15	9.86
20	9.9	0.6	0.2	0.84	0.05	0.15	9.86
30	11.3	0.8	0.2	0.96	0.07	0.15	9.85
45	11.1	0.7	0.2	0.94	0.06	0.15	9.76
60	12.0	1.0	0.2	1.02	0.09	0.15	9.61
120	14.6	1.3	0.3	1.24	0.11	0.23	9.57
240	28.1	2.1	0.3	2.38	0.18	0.23	9.49
Washing water	4.7	0.9	0.3	0.40	0.08	0.23	-

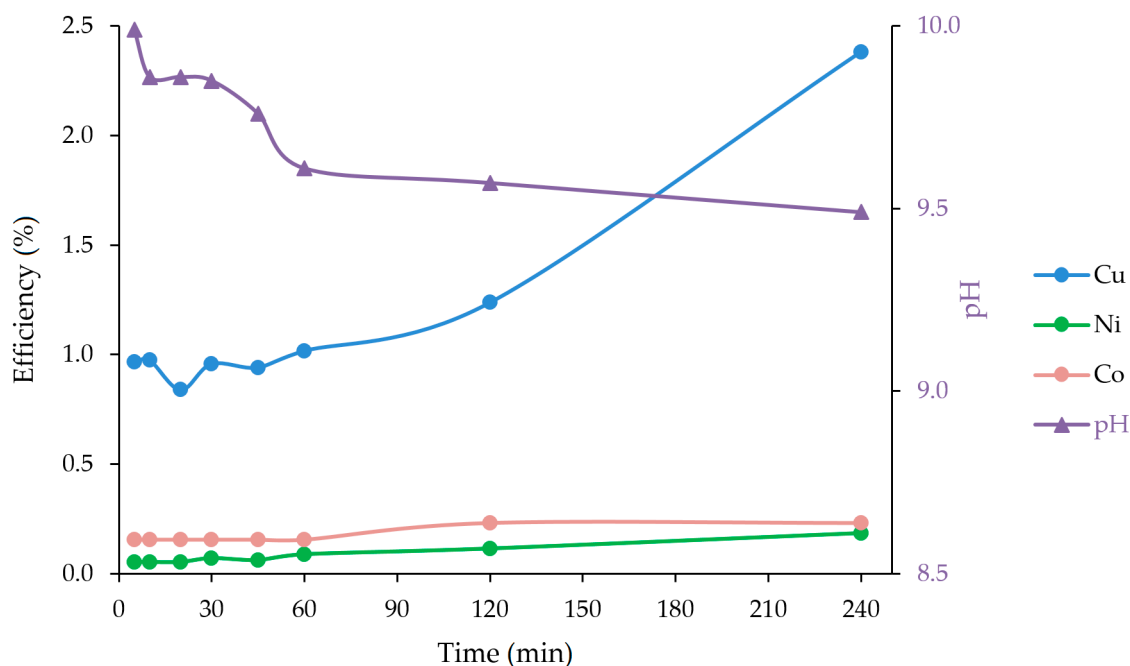


Figure 1. Kinetics of metals extraction during ammoniacal leaching at room temperature.

During ammonia leaching at 50 °C, the metals concentrations in the solution increased significantly (Table 3, Figure 2). It can be deduced from Table 3 and Figure 2 that the concentration of copper, nickel, and cobalt increased almost linearly with the increasing leaching time. After four hours of leaching, 565 mg/L of copper, 223 mg/L of nickel, and 10.7 mg/L of cobalt were detected in leaching liquors, corresponding to the extraction efficiencies of 47.9% of Cu, 19.6% of Ni, and 8.2% of Co.

Table 3. Metals concentration and extraction efficiency of ammoniacal leaching at 50 °C.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	123	4.6	0.8	10.4	0.40	0.62	10.00
10	180	5.5	0.8	15.3	0.48	0.62	9.95
20	192	7.5	0.8	16.3	0.66	0.62	9.66
30	232	9.5	0.8	19.7	0.83	0.62	9.65
45	244	12.3	0.8	20.7	1.08	0.62	9.52
60	290	19.1	0.8	24.6	1.68	0.62	9.56
90	329	35.2	1.0	27.9	3.09	0.77	9.39
120	409	87.6	2.9	34.7	7.68	2.23	9.26
150	444	114	4.5	37.6	10.00	3.46	9.14
180	484	152	7.4	41.0	13.33	5.69	9.05
210	553	219	9.4	46.9	19.21	7.23	8.94
240	565	223	10.7	47.9	19.56	8.23	8.86
Washing water	55.9	26.6	0.4	4.7	2.33	0.31	-

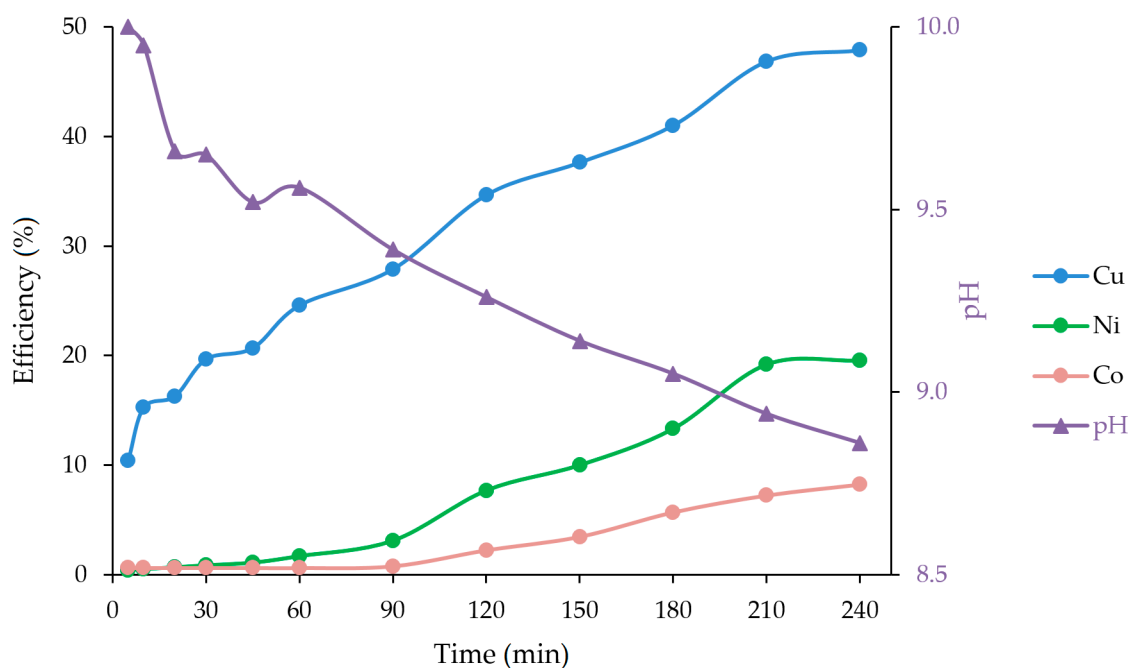


Figure 2. Kinetics of metals extraction during ammoniacal leaching at 50 °C.

During ammoniacal leaching at 85 °C, the leaching process was faster (Table 4, Figure 3). The concentration of metals in the leachate began to decline after a certain period of leaching: copper after 60 min, nickel after 90 min, and cobalt after 45 min. This finding suggests that the extraction efficiency of copper, nickel, and cobalt after the peak gradually decreases over the time of leaching, which may be due to their adsorption on nodules or due to the formation of metal sulfides from the decomposition of thiosulfate at high temperature [14].

Table 4. Metals concentration and extraction efficiency of ammoniacal leaching at 85 °C.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	349	147	13.5	29.6	12.9	10.38	9.37
10	392	199	20.0	33.2	17.5	15.38	9.37
20	446	254	24.5	37.8	22.3	18.85	9.17
30	502	318	27.6	42.5	27.9	21.23	9.14
45	548	398	31.1	46.4	34.9	23.92	8.93
60	580	428	27.5	49.2	37.5	21.15	8.73
90	343	479	18.6	29.1	42.0	14.31	8.60
120	93	451	14.5	7.9	39.6	11.15	8.55
Washing water	96.5	139	6.0	8.2	12.2	4.62	-

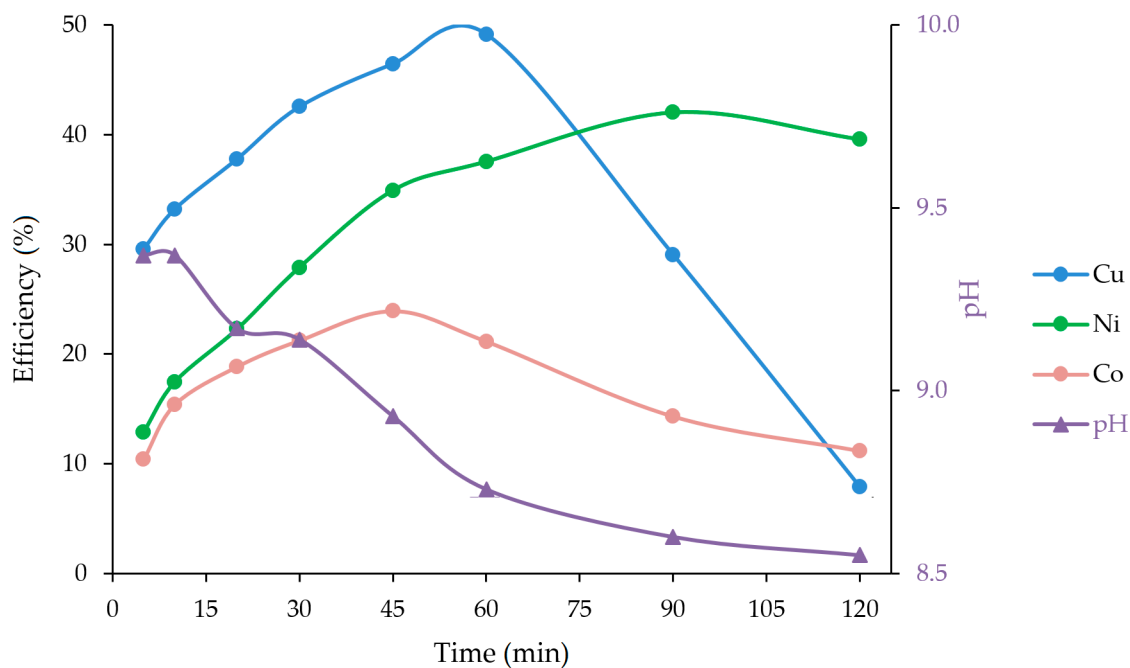


Figure 3. Kinetics of metals extraction during ammoniacal leaching at 85 °C.

3.2. Ammoniacal Leaching with Ultrasound

The results of ultrasound-assisted ammoniacal leaching at room temperature indicate that the amount of extracted metals in solution did not change over the studied leaching duration (Table 5, Figure 4). Cobalt and/or nickel were not extracted significantly. Therefore, this method could offer the selective leaching of copper.

Table 5. Metals concentration and extraction efficiency of ammoniacal leaching with ultrasound at room temperature.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	108	1.3	1	9.2	0.11	0.77	9.84
10	119	1.5	1	10.1	0.13	0.77	9.81
20	117	1.5	1	9.9	0.13	0.77	9.71
30	127	1.6	1	10.8	0.14	0.77	9.64
45	121	1.7	1	10.3	0.15	0.77	9.57
60	111	1.7	1	9.4	0.15	0.77	9.46
120	101	2.0	1	8.6	0.18	0.77	9.23
240	105	3.0	1	8.9	0.26	0.77	9.01
Washing water	23.8	1.1	0.5	2.0	0.10	0.38	-

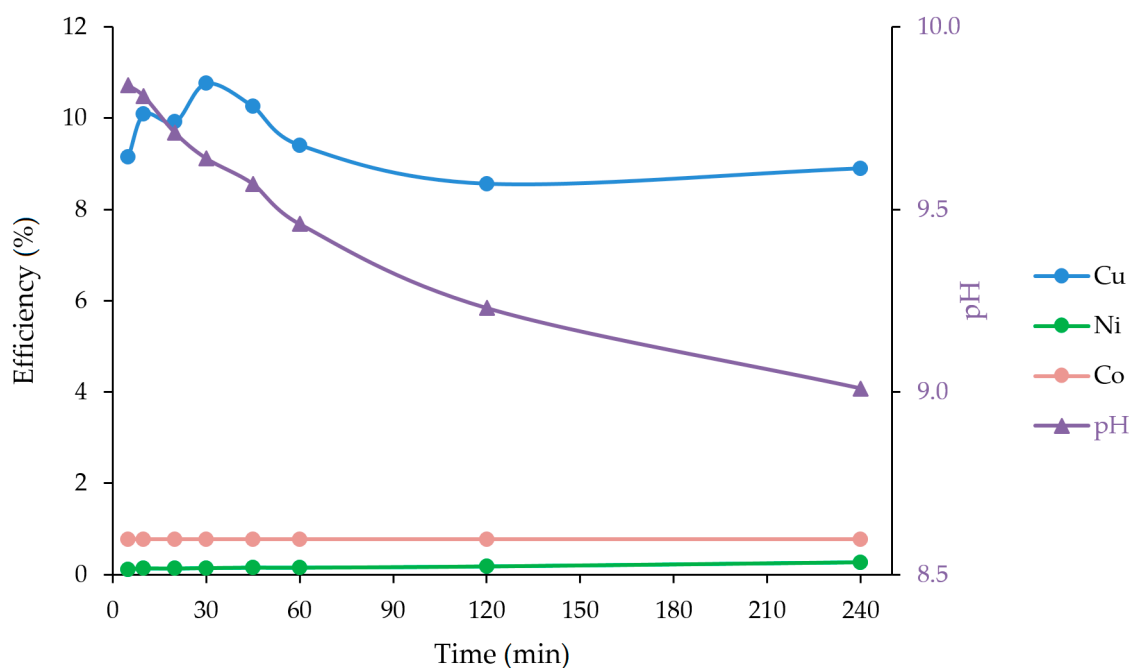


Figure 4. Kinetics of metals extraction during ammoniacal leaching with ultrasound at room temperature.

During ultrasonic ammoniacal leaching at 50 °C, the extraction efficiencies of copper and nickel were higher than at room temperature, and the amount of cobalt again was minimal (Table 6, Figure 5). It can be deduced from the table and graph that the concentrations of copper and nickel increased almost linearly with the leaching time.

Table 6. Metals concentration and extraction efficiency of ammoniacal leaching with ultrasound at 50 °C.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	197	3.9	0.4	16.7	0.34	0.31	9.70
10	213	4.7	0.4	18.1	0.41	0.31	9.67
20	255	7.4	0.4	21.6	0.65	0.31	9.55
30	272	9.2	0.4	23.1	0.81	0.31	9.49
45	312	16.6	0.5	26.4	1.46	0.38	9.31
60	350	25.5	0.5	29.7	2.24	0.38	9.19
90	441	53.6	0.6	37.4	4.70	0.46	8.96
120	490	78.3	0.6	41.5	6.87	0.46	8.95
150	523	118	0.7	44.3	10.35	0.54	8.94
180	581	155	0.9	49.2	13.60	0.69	8.85
210	624	202	1.1	52.9	17.72	0.85	8.79
240	668	247	1.8	56.6	21.67	1.38	6.86
Washing water	33.9	16.6	0.1	2.9	1.46	0.08	-

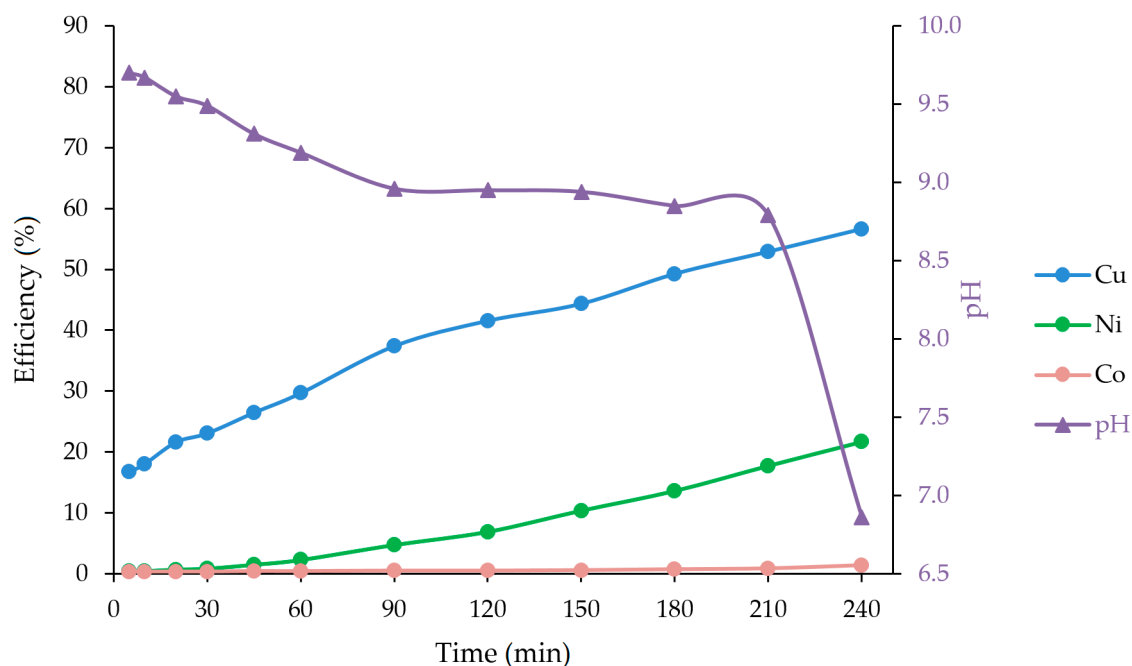


Figure 5. Kinetics of metals extraction during ammoniacal leaching with ultrasound at 50 °C.

During ammoniacal ultrasonic leaching at 85 °C, the leaching process was faster than leaching without ultrasonication at the same temperature (Table 7, Figure 6). Although after 90 min of leaching, the concentration of copper and cobalt in the leaching liquor started decreasing. A decrease in the nickel concentrations was not observed. After three hours, a selective nickel extraction was achieved.

Table 7. Metals concentration and extraction efficiency of ammoniacal leaching with ultrasound at 85 °C.

Time (min)	Concentration (mg/L)			Efficiency (%)			pH
	Cu	Ni	Co	Cu	Ni	Co	
5	401	118	2.7	34.0	10.4	2.08	9.16
10	512	229	5.1	43.4	20.1	3.92	8.90
20	632	364	14.3	53.6	31.9	11.00	8.69
30	677	443	25.1	57.4	38.9	19.31	8.48
45	717	545	32.6	60.8	47.8	25.08	8.36
60	817	619	35.1	69.2	54.3	27.00	8.41
90	978	808	42.0	82.9	70.9	32.31	7.40
120	551	856	36.0	46.7	75.1	27.69	7.30
150	52	836	21.9	4.4	73.3	16.85	7.23
180	7	827	11.5	0.6	72.5	8.85	7.33
210	32	855	6.5	2.7	75.0	5.00	7.00
Washing water	23.2	64.6	1.0	2.0	5.7	0.77	-

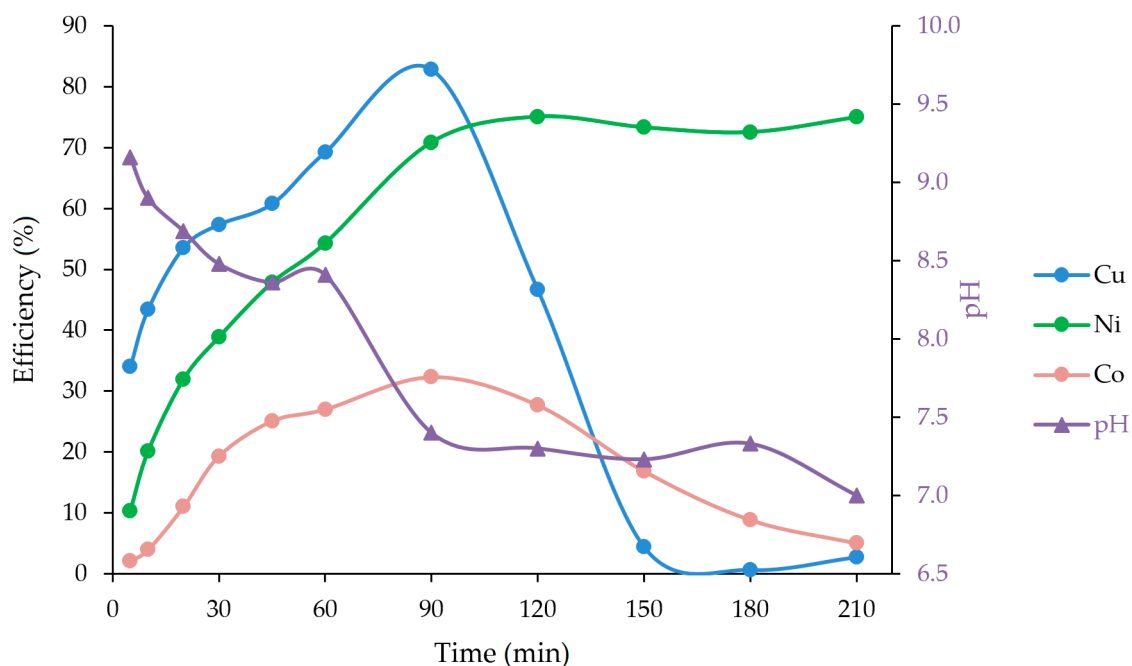


Figure 6. Kinetics of metals extraction during ammoniacal leaching with ultrasound at 85 °C.

3.3. Ammoniacal Leaching with Microwave

During ammoniacal leaching with microwaves at the output power of 30 W, an increased metals concentration in the leachate was achieved (Table 8, Figure 7). Overall, a comparable amount of metals was extracted as with the ammoniacal leaching at 50 °C. A reduction of pH to the acidic area, where the thiosulfate decomposes, was observed.

Table 8. Metals concentration and extraction efficiency of ammoniacal leaching with microwave (30 W).

Time (min)	Concentration (mg/L)			Efficiency (%)			Temperature (°C)
	Cu	Ni	Co	Cu	Ni	Co	
5	76.5	1.3	0.2	6.5	0.11	0.15	39
10	86.6	1.4	0.2	7.3	0.12	0.15	45
20	88.5	2.4	0.4	7.5	0.21	0.31	58
30	95.2	6.0	0.8	8.1	0.53	0.62	65
45	130	15.4	1.2	11.0	1.35	0.92	63
60	164	24.8	1.2	13.9	2.18	0.92	63
90	200	39.1	1.5	16.9	3.43	1.15	64
120	254	59.8	2.2	21.5	5.25	1.69	63
150	315	90.0	3.4	26.7	7.89	2.62	60
180	372	117	4.4	31.5	10.26	3.38	62
210	416	153	6.5	35.3	13.42	5.00	62
240	499	200	9.2	42.3	17.54	7.08	60
Washing water	79.7	30.5	1.1	6.8	2.68	0.85	-

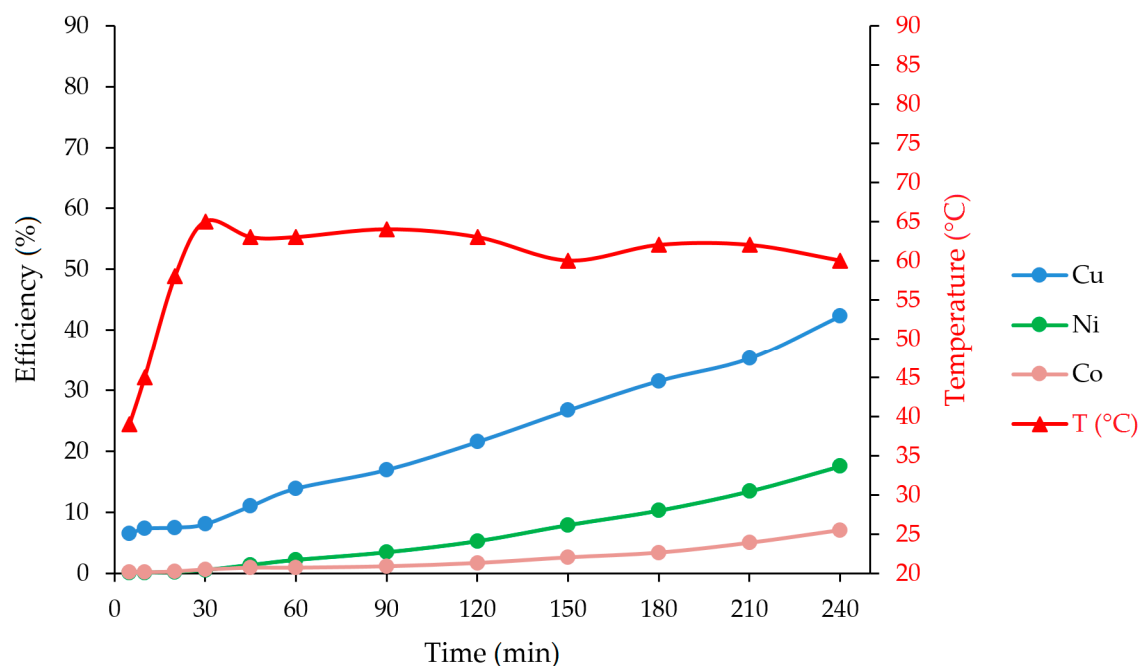


Figure 7. Kinetics of metals extraction during ammoniacal leaching with microwave (30 W).

During ammoniacal leaching with microwaves at the output power of 60 W, higher metals extraction took place, compared with that at 30 W (Table 9, Figure 8). Nevertheless, the metals concentration in the leaching liquor started decreasing after the leaching temperature reached 70 °C. A significant reduction of pH to the acidic area (pH = 2.5–3), where the thiosulfate decomposes, was observed.

Table 9. Metals concentration and extraction efficiency of ammoniacal leaching with microwave (60 W).

Time (min)	Concentration (mg/L)			Efficiency (%)			Temperature (°C)
	Cu	Ni	Co	Cu	Ni	Co	
5	95.7	1.2	0.3	8.1	0.11	0.23	32
10	117	1.5	0.2	9.9	0.13	0.15	39
20	151	2.2	0.3	12.8	0.19	0.23	49
30	187	4.4	0.3	15.8	0.39	0.23	58
45	249	19.5	0.5	21.1	1.71	0.38	62
60	350	81.9	1.8	29.7	7.18	1.38	66
90	608	255	10.4	51.5	22.37	8.00	71
120	700	357	17.3	59.3	31.32	13.31	73
150	774	436	19.1	65.6	38.25	14.69	76
180	772	544	14.6	65.4	47.72	11.23	75
210	787	550	10.9	66.7	48.25	8.38	81
240	663	430	7.6	56.2	37.72	5.85	81
Washing water	219	171	2.3	18.6	15.00	1.77	-

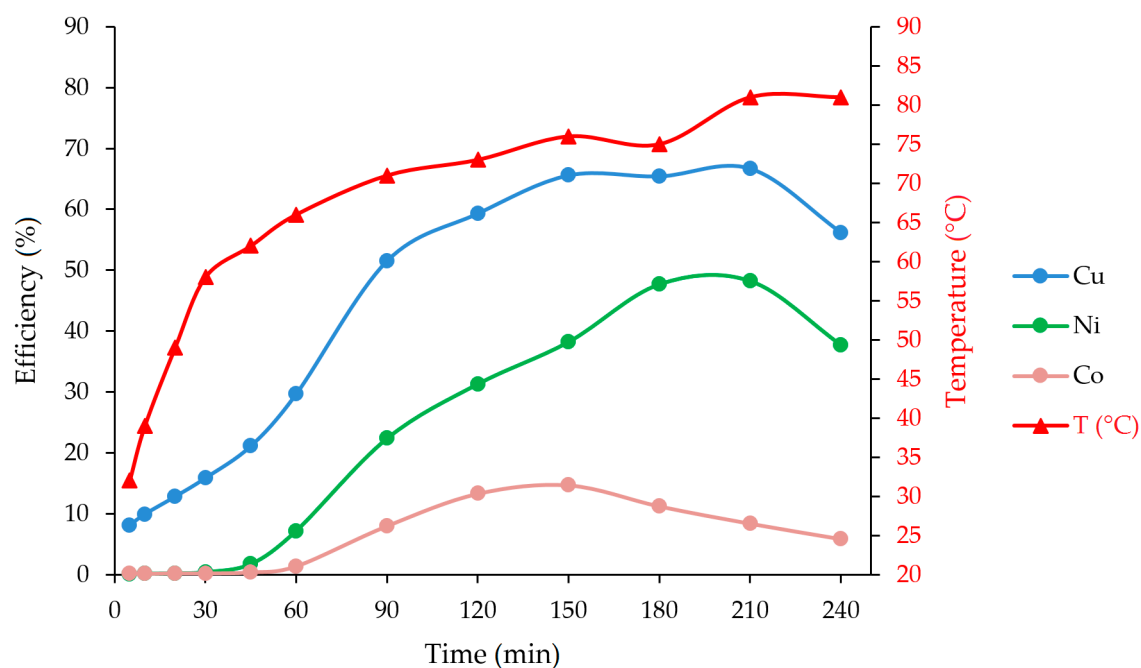


Figure 8. Kinetics of metals extraction during ammoniacal leaching with microwave (60 W).

3.4. Ammoniacal Leaching with Ultrasound and Microwave

During ammoniacal leaching with ultrasound and microwaves with the output power of 30 W, an increase in the metals concentration in the leachate was observed (Table 10, Figure 9). Ultrasound improved the extraction of copper and nickel, compared with leaching with only microwaves. The temperature increased gradually to 70 °C.

Table 10. Metals concentration and extraction efficiency of ammoniacal leaching with ultrasound and microwave (30 W).

Time (min)	Concentration (mg/L)			Efficiency (%)			Temperature (°C)
	Cu	Ni	Co	Cu	Ni	Co	
5	175	1.8	0.4	14.8	0.16	0.31	23
10	182	2.0	0.4	15.4	0.18	0.31	26
20	197	2.1	0.4	16.7	0.18	0.31	29
30	202	2.2	0.4	17.1	0.19	0.31	33
45	230	2.6	0.4	19.5	0.23	0.31	36
60	250	2.9	0.4	21.2	0.25	0.31	42
90	302	5.2	0.5	25.6	0.46	0.38	50
120	354	10.5	0.5	30.0	0.92	0.38	54
150	455	49.5	0.7	38.6	4.34	0.54	62
180	528	141	1.3	44.7	12.37	1.00	67
210	611	274	3.0	51.8	24.04	2.31	70
240	656	336	4.5	55.6	29.47	3.46	70
Washing water	263	154	1.5	22.3	13.51	1.15	-

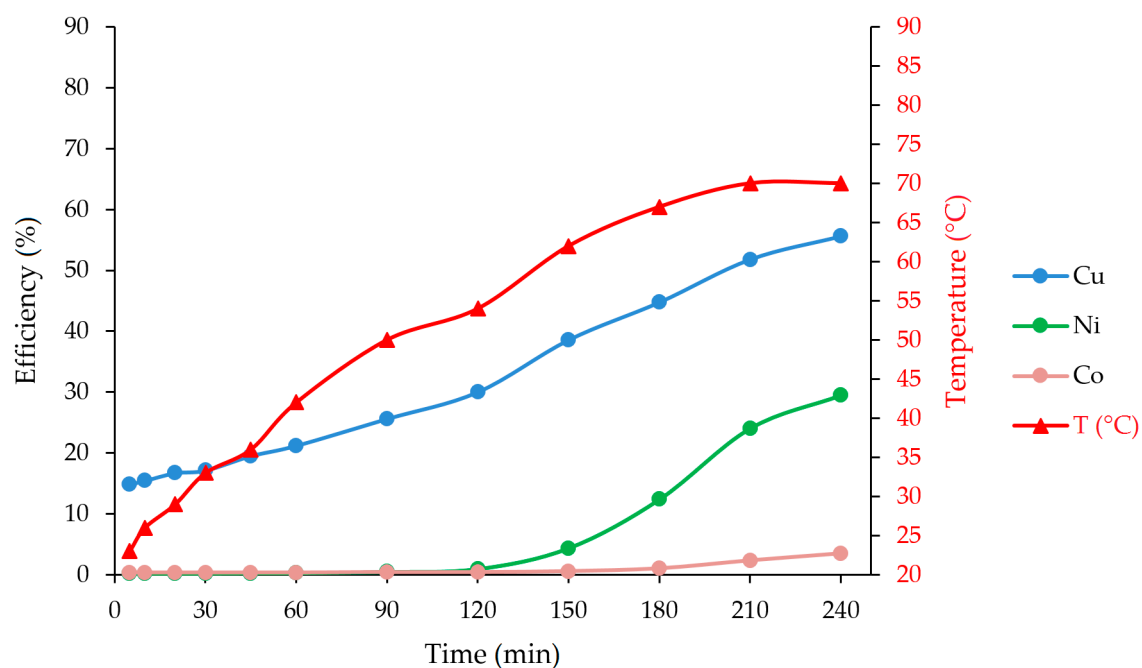


Figure 9. Kinetics of metals extraction during ammoniacal leaching with ultrasound and microwave (30 W).

During ammoniacal leaching with ultrasound and microwaves at the output power of 60 W, a further increase in the metals concentration in the leachate was observed (Table 11, Figure 10). The temperature again increased gradually to 90 °C.

Table 11. Metals concentration and extraction efficiency of ammoniacal leaching with ultrasound and microwave (60 W).

Time (min)	Concentration (mg/L)			Efficiency (%)			Temperature (°C)
	Cu	Ni	Co	Cu	Ni	Co	
5	110	1.5	0.2	9.3	0.13	0.15	33
10	118	1.7	0.2	10.0	0.15	0.15	44
20	173	5.6	0.3	14.7	0.49	0.23	62
30	248	19.4	0.5	21.0	1.70	0.38	65
45	369	115	2.0	31.3	10.09	1.54	74
60	658	392	9.0	55.8	34.39	6.92	82
120	721	489	20.0	61.1	42.89	15.38	89
240	744	545	22.4	63.1	47.81	17.23	89
Washing water	204	144	7.0	17.3	12.63	5.38	-

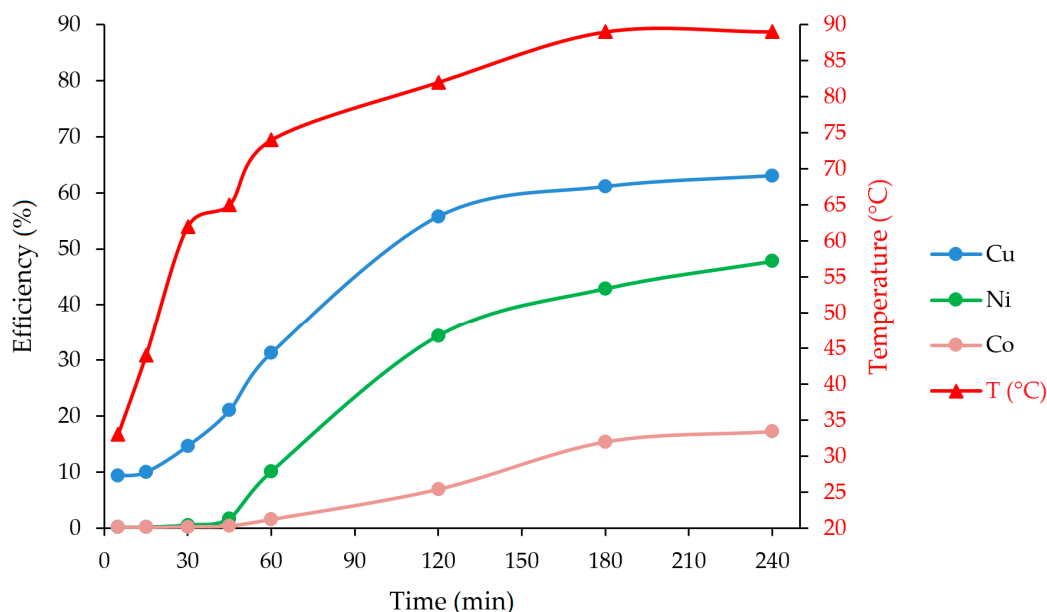


Figure 10. Kinetics of metals extraction during ammoniacal leaching with ultrasound and microwave (60 W).

4. Discussion

The extraction efficiency of Cu, Ni, and Co from deep-sea nodules by ammoniacal leaching at room temperature is very low (Figure 1). Using ultrasound, the Cu extraction efficiency was nearly ten-fold, but after four hours of leaching, it still did not exceed 10%. Cobalt and nickel require a higher temperature for their extraction from deep-sea manganese nodules in the ammoniacal environment, and in the presence of the ammonium thiosulfate as the reducing agent.

During ammoniacal leaching at 50 °C, the metals concentration in leaching liquors significantly increased in comparison with the previous leaching tests at room temperature. The extraction efficiency of Cu, Ni, and Co was almost 50%, 20%, and around 10%, respectively. Using ultrasound, a higher extraction of copper was achieved, but the extraction of cobalt was minimal. The amount of nickel was the same as that from ammoniacal leaching.

During ammoniacal leaching at 85 °C, a high amount of copper, nickel, and cobalt was extracted. The extraction of copper, nickel, and cobalt decreases for a longer leaching time, which may be due to adsorption on nodules or due to the formation of metal sulfides from the decomposition of thiosulfate [14]. The concentration of copper, nickel, and cobalt in the leachate began to decline after 60, 90, and 45 min, respectively. The extraction efficiency of all metals at 85 °C in the presence of ultrasound reached the highest values of all measurements, namely 83% for copper, 75% for nickel, and cobalt leaching efficiency was more than 32% after about 90 min of leaching. After 90 min of leaching, the nickel extraction achieved the steady state, but copper and cobalt extraction began decreasing with increasing leaching time. After 210 min, the copper and cobalt concentration in leaching liquors was minimal. This finding can be used to achieve a selective leaching of nickel from deep-sea nodules.

According to the E-pH diagram of the Cu–NH₃–H₂O system [29], it is presumed that the decomposition of copper ammine complexes occurs when the pH decreases. Excluded copper cations react with the hydroxide anions to form copper (I) hydroxide, which is practically insoluble. That results in a significant decrease of copper in leachate after the decreasing of pH.

During ammoniacal leaching with microwaves with the output power of 30 W, the temperature in the reaction vessel increased to 65 °C. The extraction efficiency after four hours was 42% for copper, 17.5% for nickel, and 7% for cobalt. When a combination of ultrasound and microwave was used, the temperature reached 70 °C. The extraction efficiency of copper increased to 54% and to 30%

for nickel. However, the cobalt extraction efficiency remained below 10%. The decrease in metals concentration at longer leaching duration was not observed.

During ammoniacal leaching with microwaves with the output power of 60 W, the leaching temperature increased above 80 °C. The metals extraction is higher. The maximum extraction efficiency was 67% for copper, 48% for nickel, and 15% for cobalt. Using a combination of ultrasound and microwaves, the temperature increases to 89 °C and metals extraction efficiencies remained similar to those achieved by leaching with microwaves of the output power of 60 W without ultrasound. Thus, ultrasound did not have a significant effect on the extraction efficiency.

5. Conclusions

The ammoniacal leaching process in the presence of ammonium thiosulfate was used for the extraction of non-ferrous metals, especially copper, nickel, and cobalt, from polymetallic manganese nodules. It was found, that higher leaching temperature increases the metals extraction efficiency. In the combination with ultrasound, the reductive ammoniacal leaching results in higher metals extraction at the same leaching temperatures, compared with leaching without ultrasound. The effect of microwaves on metals extraction is insignificant. During leaching with ultrasound at 85 °C and/or leaching with microwaves of the output of 60 W, the decrease of metals extraction was observed over a longer leaching duration. This observed decrease in metals extraction was probably the result of the formation of metals sulfides from the decomposition of thiosulfate at high temperatures. On the other hand, during the ultrasonic reductive ammoniacal leaching at 85 °C, the extraction of nickel did not follow the decreasing course, observed in the extraction of copper and cobalt. The finding suggests that nickel can be selectively extracted from the nodules if ultrasonic leaching was carried out at 85 °C for 210 min. The maximal extraction efficiency of copper, nickel, and cobalt was 83%, 71%, and 32%, respectively when the reductive ammoniacal leaching was carried out at 85 °C for 90 min in the presence of ultrasound. The microwaves-assisted reductive ammoniacal leaching provides the maximal extraction efficiency of copper, nickel, and cobalt of 67%, 48%, and 8%, respectively, when the output power was 60 W and leaching time was 210 min.

Author Contributions: A.K. compiled the paper and did measurements. H.N.V. worked as a scientific supervisor, designed the experiments, and ensured an evaluation of results. P.D. helped with the measurements and constructed the apparatus.

Funding: This research was partly funded by InterOcean Metals Joint Organization, Szczecin, Poland under international grant No. 106190063.

Acknowledgments: The authors would like to say thank you for Jana Selucka for her supporting role in carrying out the AAS analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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