Article

Study on Ultrasonically-Enhanced Sulfuric Acid Leaching of Nickel from Nickel-Containing Residue

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Abstract: In this paper, nickel-containing residue, a typical solid waste produced in the battery production process, was used to study the cavitation characteristics of ultrasonic waves in a liquid–solid reaction. The ultrasonically-enhanced leaching technology for multicomponent and complex nickel-containing residue was studied through systematic ultrasonic-conventional comparative experiments. An ultrasonic leaching kinetics model was established which provided reliable technological guidance and basic theory for the comprehensive utilization of nickel-containing residue. In the study, it was found that ultrasonically-enhanced leaching for 40 min obtained the same result as conventional leaching for 80 min, and the Ni extraction degree reached more than 95%. According to the kinetic fitting of the leaching process, it was found that the sulfuric acid leaching process belonged to the diffusion-controlled model of solid product layers under conventional and ultrasonic conditions, and the activation energy of the reaction was $E_{a1} = 17.74$ kJ/mol and $E_{a2} = 5.04$ kJ/mol, respectively.

Keywords: leaching; ultrasound; nickel-containing residue

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1. Introduction

In recent years, with the rapid development of the battery industry, the amount of wastewater containing heavy metals produced by battery enterprises is increasing [1]. At present, a chemical precipitation method is commonly used to treat the wastewater where the heavy metal ions are transferred to the waste residue, thus forming a multi-component hazardous waste containing Ni, Cd, Fe, Cu, Ca, and other metals [2,3]. The nickel in the residue produced by battery enterprises typically exists in the form of a hydrate. The nickel content in the residue is generally about 10 wt %, and its elemental content is much higher than that of the ore, so it has a high utilization value.

Nickel-containing residue is unfortunately easily accumulated, unstable, and dissolves easily in water. If it is not treated or contained, it will cause serious pollution issues in soil and groundwater and will result in further damage to human health and the environment [4,5]. Many researchers have worked on the comprehensive treatment of waste residue containing heavy metals and have rapidly developed methods in recent years, resulting in encouraging progress [6,7]. Among the developed methods, the recovery of heavy metals through sulfuric acid leaching or ammonia leaching are key points in these studies, as well as other ways to selectively recover valuable metals [8,9].

The acid-leaching method is an effective leaching method. Silva et al. [10] studied the leaching of sludge from a nickel plating plant using a sulfuric acid medium and an ammonia medium. The maximum nickel conversion was 98.0% under the following experimental conditions: 100 g/L acid concentration, 5:1 liquid–solid ratio, particle size less than 1 mm, digestion time 1 h, stirring speed 700 rpm (all at room temperature and atmospheric pressure). Nickel could be extracted without Cr using an ammonia medium, but the nickel conversion rate was only 50%, which is much lower than that of sulfuric acid leaching. This was because the metals in the sludge mainly existed in the form of oxides

or hydroxides. Therefore, by adding acid to the electroplating sludge, most of the metals dissolved by forming soluble ions or coordination ions. Su et al. [11] studied the effect of leaching valuable metals from the electroplating sludge under acidic conditions and found that the leaching rate of copper was as high as 80.6% when the concentration of phosphate participation in hydrochloric acid medium was 1.5 mol/L, the liquid–solid ratio was 10:1, and the temperature was 40 °C. By adding stearyltrimethyl ammonium chloride (STAC), Zhang et al. [12] improved the ion diffusion, and thus the leaching rate of Ni increased from 64.9% to 74.1% after 6 h of leaching in 8 wt % sulfuric acid, and with a liquid–solid ratio (v/w) of 10 at 90 °C.

The recovery of valuable metals from nickel-containing residue generally requires certain temperature conditions, harsh operating conditions, a large amount of acid, and leaves a large amount of acid waste. Therefore, it is necessary to develop a new process with milder conditions and high efficiency.

Since the first International Symposium on Sonochemistry was held in the U.K. in 1986, ultrasound has attracted much attention as an important means of enhancing the leaching process [13–15]. When the ultrasonic intensity is high enough, cavitation will occur. During cavitation, bubbles in the solution form, oscillate, grow, shrink, and finally collapse, all within a short time and a small space. This process produces a temperature of more than 5000 K and a pressure of about 5×10^7 Pa, accompanied by a strong shock wave [16–18]. When the ultrasonic intensity is insufficient to produce cavitation, the mechanical effect strongly agitates the liquid, reduces the diffusion resistance, destroys the boundary layer, and therefore accelerates the mass and heat transfer [14].

In light of the difficult treatment of lead in an electrolytic manganese anode sludge, Xie et al. [19] proposed a method combining a conventional roasting pretreatment with an ultrasonically enhanced leaching of ammonium acetate. They found that both conventional and ultrasonic leaching processes were controlled by diffusion, and the activation energies of conventional and ultrasonic leaching processes were 29.40 kJ/mol and 26.95 kJ/mol, respectively. Nivetha et al. [20] used a sulfuric acid solvent as the leaching agent to extract nickel ions from spent batteries and found that the leaching rate after ultrasonic-assisted leaching was 98.5%, and the rate after conventional leaching was 90.8%. Gui et al. [21] studied the influence of ultrasonic waves on the leaching of gold and found that under ultrasonic conditions, the gold leaching speed was eight times as fast as that under conventional conditions, and the leaching rate was increased by about 25%. Additionally, the activation energy decreased from 22.65 kJ/mol to 13.86 kJ/mol.

In this paper, the nickel-containing residue produced from battery manufacturing was used as raw material, and the ultrasonic method was used to supplement an acid leaching process. The effects on the reaction temperature, mass fraction of acid, and the ratio of liquid to solid on the Ni extraction degree were investigated to obtain more suitable process parameters. This study was completed to find a more efficient, environmentally friendly, and economic nickel leaching process.

2. Materials and Methods

2.1. Raw Materials

In this study, nickel-containing residue produced by the chemical precipitation of wastewater from a battery manufacturing enterprise in Henan, China, was used as the raw material. Figures 1 and 2 show the major components and microstructure of the sample after pretreatment as reported in our earlier study [22,23]. After pretreating the sample via roasting, the gaspeite and nickel hydroxide hydrate in the residue was found to be transformed into bunsenite without altering the major species of the other metal elements in the residue. A reduction of the weight of the residue by more than 20% was observed (1 g of dried nickel-containing residue was roasted at 1000 °C for 1 h, the measured LOI (loss on ignition) value of nickel-containing residue was 43.57%). As shown in Figure 1, calcite was found to be the major component, and Ni mainly existed in bunsenite, while small

amounts of quartz and magnesium silicate were also present. It can be seen in Figure 2 that the surface of the sample particles was rough and the microscopic shape was irregular

Figure 1. X-ray diffraction pattern of the nickel-containing residue.

Figure 2. SEM of the residue after pretreatment.

Table 1 shows the chemical composition of the nickel-containing residue determined by mineralogical analysis and X-ray fluorescence. The residue mainly contained 35.88% CaO, 16.21% MgO, 13.81% NiO, 8.02% Fe₂O₃, 5.07% SiO₂, and 1.05% CdO.

Table 1. The main components of the nickel-containing residue.

Composition	CaO	MgO	NiO	Fe ₂ O ₃	SiO ₂	CdO	Al ₂ O ₃	ZnO
Content (wt %)	35.88	16.21	13.81	8.02	5.07	1.05	1.01	0.63

2.2. Experimental Methods and Devices

Conventional leaching: 10 g of the residue having different particle sizes (−250, −180, −150, −120, −109, −96, and −80 µm) was weighed into a 150 mL circular beaker. Sulfuric acid having different mass fractions (5%, 10%, 15%, and 20%) was added into the beaker in different specific solid–liquid ratios (1:5, 1:6, 1:7, 1:8, and 1:9) and the beaker was placed into a thermostatic water bath equipped with a magnetic stirrer. The residue was treated for different time intervals from 0–80 min under different temperatures (25, 35, 45, and 55 °C) using a stirring speed of 150 rpm.

Ultrasonic leaching: The details of the treatment procedure were similar to the conventional leaching described above other than the fact that the samples were treated in an ultrasonic bath having different ultrasonic power levels (300, 400, 500, 600, 700, and 800 W) for 0–45 min.

Characterization: In order to determine the extent of nickel leaching, the leached solution was analyzed for its nickel content before and after the leaching via inductively coupled plasma optical emission spectrometry (ICP, Agilent5100, Agilent Technologies, Palo Alto, CA, USA). Changes of the microstructure and phase after leaching were analyzed by SEM-EDS (SPM-S3400N, Hitachi, Tokyo, Japan) and X-ray powder diffraction (XRD) (XRD-7000S/L, Shimadzu, Kyoto, Japan), respectively. Particle size of the leached residue was analyzed by laser particle size distribution tester (Mastersizer 3000, Malvern, England). The specific surface area of the leached slag was determined by a specific surface area analyzer (BET) (ASAP 2460, Micromeritics, Shanghai, China).

Experimental device: The ultrasonic leaching system used in the experiment was a self-developed ultrasonic leaching system based on reported literature [15]. A schematic of the system is shown in Figure 3. The device consists of an ultrasonic generator (QHY-1200, Wuxi, China) which was composed of a quartz probe with a diameter of 8 mm and a thermostatic water bath equipped with a magnetic stirrer (DK-98-IIA, Tianjing, China). The leaching temperature was controlled within ± 2 °C.

Figure 3. The ultrasonically enhanced leaching system.

2.3. Data Analysis and Mathematical Modeling

As shown in Figure 1, calcite was found to be the major component, and Ni mainly existed in bunsenite. The reaction between bunsenite, calcite, and sulfuric acid:

Using the results obtained in the present work and assuming reaction (1), the kinetics of the leaching process can be evaluated. The shrinking core model can be used to describe the kinetics of heterogeneous reactions in non-porous materials. When the control step is internal diffusion, the process can be expressed as:

$$1 - 2/3x - (1 - x)^{2/3} = k_d t \quad (3)$$

where x is the Ni extraction degree (%), k_d is the diffusion velocity constant, and t is the reaction time (min).

When the control step is a surface chemical reaction, the process can be expressed as:

$$1 - (1 - x)^{1/3} = k_c t \quad (4)$$

where x is the Ni extraction degree (%), k_c is the surface chemical reaction rate constant, and t is the reaction time (min).

Dickinson and Heal [24] proposed a new modification of the shrinking core model which may be preferable for describing the kinetics of leaching reactions controlled by the interfacial transfer and internal diffusion:

$$1/3 \ln(1 - x) + (1 - x)^{-1/3} - 1 = k_b t \quad (5)$$

where x is the Ni extraction degree (%), k_b is the apparent rate constant, and t is the reaction time (min).

The activation energy of the reaction was calculated according to the Arrhenius equation.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

E_a is the activation energy (kJ/mol), A is the pre-exponential coefficient, R is the gas constant 8.314×10^{-3} kJ/(mol·K), and T is the reaction temperature (K).

The calculation of the Ni extraction degree can be expressed as:

$$\text{Ni}(\%) = \frac{m_{\text{Ni},0} - m_{\text{Ni}}}{m_{\text{Ni},0}} \quad (7)$$

where, $m_{\text{Ni},0}$ is the nickel content in the residue, and m_{Ni} is the nickel content in the leached residue.

3. Results

3.1. Effect of Leaching Temperature

As seen in Figure 4, there was a continuous increase in the Ni extraction degree in the studied temperature range. As the temperature increased, the movement of solute or solvent molecules in the leaching system was accelerated, resulting in an accelerated leaching speed and an increase in the leaching rate. In the presence of ultrasonic conditions, the leaching rate of 25 °C temperature for 40 min showed the same value for 55 °C temperature under conventional conditions over a period of 80 min, with the Ni extraction degree reaching about 95%. By comparing Figure 4a,b, it was seen that the influence of temperature on the Ni extraction degree under ultrasonic conditions was significantly smaller than that under conventional conditions. In general, an increase in reaction temperature resulted in ion diffusion through the solid masses. However, under ultrasonic conditions, there was solid surface exfoliation and production of ultrasonic cavitation micro jets which reduced the diffusion layer thickness, increased the particle surface area, and therefore greatly improved the internal diffusion of reactive ions. Hence, the Ni extraction degree was less sensitive to increasing temperatures under ultrasonic conditions. In order to achieve high leaching rate while saving energy, the ultrasonic leaching process of 40 min at 25 °C temperature was selected for further studies.

Figure 4. Influence of the temperature on the Ni extraction degree. (a) Conventional: mass fraction of sulfuric acid = 15%, solid-liquid ratio = 1:7, particle size = −150 μm, stirring speed = 150 rpm; (b) ultrasonic: mass fraction of sulfuric acid = 15%, solid-liquid ratio = 1:7, particle size = −150 μm, ultrasonic power = 600 W.

3.2. Effect of Sulfuric Acid Concentration

It can be seen in Figure 5 that the Ni extraction degree increased with the increase in the mass fraction of sulfuric acid in the studied range. This is because the solution provided additional hydrogen ions with the increase in the mass fraction of sulfuric acid, therefore, all the alkaline nickel compounds were converted to free nickel ions which improved the Ni extraction degree. By comparing Figure 5a,b, it was found that the concentration of the leaching agent had a significant effect on the conventional leaching process. In the presence of ultrasonic conditions, for 15% sulfuric acid as the leachant, the Ni extraction degree was about 95% after leaching for 40 min. Under identical conditions, ultrasound wave is able to achieve better results compared with conventional leaching in low concentration of sulfuric acid. When the concentration of this leaching agent was low, the viscosity was small, and the cavitation bubbles were easily generated. Moreover, the energy loss in the propagation process was small, which was conducive to the asymmetric bursting of the intermingling bubbles near the holes of particles, which therefore increased the diffusion and mass transfer velocity in the particles, shortened the reaction time, and improved the leaching rate. As a result, for further studies, 15% sulfuric acid was selected as the leaching agent under ultrasonic conditions.

Figure 5. The influence of sulfuric acid concentration on the Ni extraction degree. (a) Conventional: temperature = 25 °C, solid-liquid ratio = 1:7, particle size = −150 μm, stirring speed = 150 rpm; (b) ultrasonic: temperature = 25 °C, solid-liquid ratio = 1:7, ultrasonic power = 600 W, particle size = −150 μm.

3.3. Effect of Particle Size

It was seen from Figure 6 that the Ni extraction degree increased with the reduction of residue particle size, and the Ni extraction degree reached a higher level when the particle size was −150 μm under the ultrasonic conditions. In comparison, the influence of particle size on the Ni extraction degree under ultrasonic conditions was less than that under conventional conditions. The leaching rate was also proportional to the surface area of contact between liquid and solid. With the decrease in particle size, the contact area between the liquid and solid phases increased, and the internal diffusion resistance decreased, which was beneficial for improving the leaching effect of nickel. Under the ultrasonic field, cavitation bubbles had a certain peeling effect on the surface of solid particles. This effectively separated the insoluble layer on the surface of particles, resulting in constant production of new reaction interfaces, which caused a reduction in particle size during the leaching process, and reduced the impact of particle size on the leaching rate. Therefore, 150 μm was selected as the residue particle size for further studies.

Figure 6. Effect of particle size on Ni extraction degree. Conventional: leaching temperature = 25 °C, mass fraction of sulfuric acid = 15%, solid-liquid ratio = 1:7, stirring speed = 150 rpm, leaching time = 40 min. Ultrasonic: leaching temperature = 25 °C, mass fraction of sulfuric acid = 15%, solid-liquid ratio = 1:7, ultrasonic power = 600 W, leaching time = 40 min.

3.4. Effect of the Solid–Liquid Ratio

It is evident from Figure 7 that with increasing solid–liquid ratio, the Ni extraction degree increased significantly till the solid–liquid ratio reached 1:7. When the solid–liquid ratio was 1:7, the Ni extraction degree reached a maximum of 95.04%. This was because the increase in the solid–liquid ratio reduced the slurry’s viscosity and improved the reaction ion diffusion conditions. Under ultrasonic conditions, the viscosity of the solution decreased when the solid–liquid ratio increased and the ultrasonic cavitation efficiency increased, leading to an increase in the leaching efficiency. The solid–liquid ratio was therefore selected as 1:7 for this experiment.

Figure 7. Effect of particle size on Ni extraction degree. Conventional: leaching temperature = 25 °C, mass fraction of sulfuric acid = 15%, particle size = −150 μm , stirring speed = 150 rpm, leaching time = 40 min. Ultrasonic: leaching temperature = 25 °C, mass fraction of sulfuric acid = 15%, particle size = −150 μm , ultrasonic power = 600 W, leaching time = 40 min.

3.5. Influence of Ultrasonic Power

As seen from Figure 8, increasing ultrasonic power from 300 W to 600 W led to an increase in the Ni extraction degree. The pulse and cavitation generated by ultrasonic waves can greatly increase the turbulence intensity and the contact area, thus enhancing the mass transfer. When the ultrasonic power was 600 W, the Ni extraction degree can increase to above 95%, and with further increase in ultrasonic power there was very little change of the leaching rate. Higher ultrasonic power led to an acceleration of the leaching reaction of other metal elements, thus affecting the leaching of nickel. On the other hand, because of the high ultrasonic power, the cavitation bubble generated by it was too large for the cavitation effect to come into full play, so the Ni extraction degree did not increase

when the ultrasonic power was higher than 600 W. Therefore, the ultrasonic power was selected as 600 W for further experiments.

Figure 8. Influence of ultrasonic power on the Ni extraction degree. Leaching temperature = 25 °C, mass fraction of sulfuric acid = 15%, particle size = −150 μm, solid-liquid ratio = 1:7, leaching time = 40 min.

3.6. Leaching Kinetics

As seen from Figure 4, with the increase in time, the Ni extraction degree also increased, but the leaching rate was not linear with time, indicating that boundary layer diffusion was not the main control step in the acid leaching process. The experimental data were substituted into Equations (1)–(3), respectively, and the fitting results are shown in Figure 9.

Figure 9. Fitting of control steps at different temperatures.

The values of R^2 in Figure 9 show that the internal diffusion control model better described the acid leaching process than that of other models under both conventional and ultrasonic conditions.

According to the Arrhenius Equation (4), taking $\ln k_d$ as the Y-axis and T^{-1} as the X-axis, Figure 10 can be obtained.

Figure 10. The relation between k_d and T^{-1} .

According to Figure 10, the activation energies of the reaction under conventional and ultrasonic conditions were calculated as $E_{a1} = 17.74$ kJ/mol and $E_{a2} = 5.04$ kJ/mol, respectively. Under conventional and ultrasonic conditions, the diffusion coefficients for sulfuric acid leaching are shown in Equations (8) and (9), respectively.

$$K = 2.2454 \times e^{-\frac{17.74}{RT}} \quad (8)$$

$$K = 0.05674 \times e^{-\frac{5.04}{RT}} \quad (9)$$

According to Figure 5, the experimental data of the nickel leaching process at different sulfuric acid concentrations were substituted into the internal diffusion control model, and the fitting results are shown in Figure 11.

Figure 11. Fitting internal diffusion control model at different sulfuric acid concentrations.

Taking $\ln k_d$ as the Y-axis and $\ln C_0$ as the X-axis, Figure 12 was obtained.

As seen in Figure 12, the slope of the line is the kinetic series $n_1 = 0.9686$ and $n_2 = 0.7384$ under conventional and ultrasonic conditions, respectively. Therefore, the kinetic equation of the sulfuric acid leaching process can be expressed as Equations (10) and (11).

$$1 - 2/3x - (1 - x)^{2/3} = \frac{2MD'c_0^{0.9686}}{\sigma\rho r_0^2}t \quad (10)$$

$$1 - 2/3x - (1 - x)^{2/3} = \frac{2MD'c_0^{0.7384}}{\sigma\rho r_0^2}t \quad (11)$$

Figure 12. Relationship between $\ln k_d$ and $\ln C_0$.

3.7. Analysis of the Leached Residue

As seen in Figure 13 and Table 2, after sulfuric acid leaching, the main phase in the material changed from calcite to gypsum. In addition, the Ni present in the material was almost entirely leached by sulfuric acid. Therefore, this proved that it was feasible to leach nickel from battery manufacturing residue by sulfuric acid. In addition, it can be found from Table 2 that under ultrasonic conditions, the valuable metals in the nickel-containing residue were separated into the liquid phase with a higher efficiency than that of the conventional conditions.

Figure 13. XRD pattern of the residue after sulfuric acid leaching. (a) Conventional: mass fraction of sulfuric acid = 15%, particle size = $-150\ \mu\text{m}$, solid-liquid ratio = 1:7, temperature = $25\ ^\circ\text{C}$, stirring speed = 150 rpm, leaching time = 80 min; (b) ultrasonic: power = 600 W, mass fraction of sulfuric acid = 15%, particle size = $-150\ \mu\text{m}$, solid-liquid ratio = 1:7, temperature = $25\ ^\circ\text{C}$, leaching time = 40 min.

Table 2. The main components of the leached residue after conventional and ultrasonic leaching.

Composition		SO ₃	CaO	SiO ₂	Fe ₂ O ₃	NiO	MgO	Al ₂ O ₃	ZnO	CdO
Conventional	Content (wt %)	53.925	25.312	2.41	1.68	1.62	0.897	0.308	0.055	0.207
Ultrasonic	Content (wt %)	53.441	27.826	1.96	0.855	0.336	0.797	0.293	0.048	0.104

As can be seen from Figure 14a, after conventional sulfuric acid leaching of nickel, there was a microstructural change of the residue with its surface becoming smooth from rough and irregular and was covered with a small amount of floc. Moreover, these regular

shaped particles with a smooth surface tend to agglomerate. Figure 14b shows the scanning electron microscope images of the residue after sulfuric acid leaching of nickel under an ultrasonic field. Compared with Figure 14a, no agglomeration of the residue particles was observed after sulfuric acid leaching under an ultrasonic field. The stripping effect of ultrasonic cavitation led to obvious fracture marks on the boundary of the leached residue, which is conducive to elimination of the surface film of the solid reactants and enhance the mass transfer between the solution and the solid pores or micropores, thus reducing the internal diffusion resistance. The kinetic fitting results are consistent with this result. Ultrasonic treatment strengthened the leaching process and reduced the reaction activation energy.

Figure 14. SEM of residue after leaching. (a) Conventional: mass fraction of sulfuric acid = 15%, particle size = $\sim 150\ \mu\text{m}$, solid–liquid ratio = 1:7, temperature = $25\ ^\circ\text{C}$, stirring speed = 150 rpm, leaching time = 80 min; (b) ultrasonic: power = 600 W, mass fraction of sulfuric acid = 15%, particle size = $\sim 150\ \mu\text{m}$, solid–liquid ratio = 1:7, temperature = $25\ ^\circ\text{C}$, leaching time = 40 min.

EDS analysis of the granular matter with a regular shape and smooth surface showed that it was mainly CaSO_4 with a small amount of CaCO_3 , while the floc material of leached residue from conventional leaching also contained a certain amount of nickel as can be seen in Figure 15a. This was consistent with the data from other conventional leaching experiments. As shown in Figure 15b, the surface of the leaching residue under ultrasonic conditions was smooth and clean, which was composed of particles with regular shape and high dispersion.

Figure 16 shows the particle size distribution of leached residue after conventional and ultrasonic leaching. It can be found from Figure 16 that the leached residue from ultrasonic leaching have a smaller particle size than that of conventional leaching. The main reason is that the ultrasonic wave prevents the agglomeration of the leached residue in the leaching process. In addition, the high temperature and high pressure micro-jet generated by ultrasonic cavitation can peel off the particle surface, as Zhang [16] and Kumar [20] report. In addition, the specific surface of the leached residue under ultrasonic conditions is $58.9057\ \text{m}^2/\text{g}$, which is 16.25% higher than that under conventional conditions, shown in Table 3. Therefore, ultrasonic can promote the subsequent leaching process.

Figure 15. EDS analysis of the residue after leaching.

Figure 16. The particle size distribution of leached residue after conventional and ultrasonic leaching.

Table 3. Specific surface area of leached slag under conventional and ultrasonic conditions.

Sample	BET Surface Area
Ultrasonic	58.9057 m ² /g
Conventional	50.6720 m ² /g

It can be found from Table 4 that the chemical composition of the leaching solution mainly contains nickel, magnesium, and iron, and a small amount of cadmium and aluminum exists. At the same time, it can be found that the content of metal elements in the leaching solution under ultrasonic conditions is higher than conventional conditions. Chemical precipitation and solvent extraction are commonly used to separate, purify, and recover metals from the leach solution [25]. Impurity elements such as magnesium, iron, aluminum, and cadmium can be removed by precipitation and/or solvent extraction. However, in these processes, especially in the precipitation process, there are selectivity problems; meaning, if the impurities are removed at a high yield, there is also a significant loss of valuable metals [26,27]. Recently, ion exchange, an efficient impurity removal method, has been widely used in the purification of nickel containing solutions. Fernandez et al. [28] used the chelating resin (Amberlite IRC 718) to treat industrial waste leachate and found that the removal rate of Zn was 93% and the removal rate of Cd was 50%. Chiu et al. [29] successfully tested several chelating resins (iminodiacetic acid, bispicolylamine, and phosphinic acid) for the adsorption of Ni and Co from manganese containing lithium-ion battery waste leachate. Zhang et al. [30] studied the removal of impurities in the synthetic lithium-ion battery waste leachate by ion exchange method through intermittent and column experiments. Ammonomethyl phosphonic acid functional chelating resin (Lewatit TP260) can remove Fe, Al, Mn, and Cu from leachate while leaving a valuable pure mixture of Co, Ni, and Li. 99.6% pure Li + Co + Ni solution (battery grade) can be obtained by this process. Regarding the removal of magnesium in the solution, a chemical precipitation method is generally applied, such as adding sodium fluoride, or an extraction method can be also used to remove magnesium in the solution [31].

Table 4. The main chemical components in the leached solution.

Chemical Component		Ni	Mg	Fe	Cd	Al	Zn
Conventional	Content (g/L)	17.95	19.75	13.11	0.12	0.11	<0.1
Ultrasonic	Content (g/L)	18.11	21.85	13.81	0.14	0.12	<0.1

4. Conclusions

(1) It is feasible to use sulfuric acid as leaching agent to recover nickel from the nickel containing residue.

(2) More than 95% nickel can be leached under the conditions of 600 W ultrasonic power, 15% sulfuric acid concentration, particle size of less than 150 µm, solid–liquid ratio of 1:7, leaching temperature of 25 °C, and leaching time of 40 min. Under the above mentioned conditions, ultrasonic leaching can increase the Ni extraction degree from 58.26% to 95.50%. The ultrasonic process increased the Ni extraction degree by about 63.92%.

(3) Ultrasound wave greatly changes the microstructure of the leached residue particles. The particle boundary of the leached residue has obvious peeling trace, and the particle dispersion is better than that of the conventional conditions.

(4) The activation energies of the reaction under conventional and ultrasonic conditions were calculated as $E_{a1} = 17.74$ kJ/mol and $E_{a2} = 5.04$ kJ/mol, respectively.

(5) The particle size of ultrasonic leaching residue is smaller than that of conventional leaching residue. And the specific surface area of the leached residue under ultrasonic conditions is 16.25% higher than that under conventional conditions.

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