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Hydrometallurgical Recovery of Iron, Nickel, and Chromium from Stainless Steel Sludge with Emphasis on Solvent Extraction and Chemical Precipitation

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Abstract: Stainless steel has a variety of applications nowadays because of its mechanical strength and corrosion resistance. The large-scale machinery made up of stainless steel has an outstanding performance and endurance for manufacturing industries. However, stainless steel scraps accumulate with a lubricant to form sludge during the operation. To reduce the environmental hazards caused by sludge, this research attempts to construct a hydrometallurgical process to recover iron, nickel, and chromium from the sludge. The experiments could be divided into four parts. First, calcination was adopted to remove the oil and water content. The factors that have impacts on the leaching efficiency, such as the type of acid and the calcination temperature, were investigated in the second part. It was optimal that the sludge was calcined at 300 °C for 8 h and leached by 4 mol/L HCl. The results revealed that the leaching percentages of iron, nickel, and chromium were 97.6%, 98.1%, and 95.7%, respectively. In the two-stage solvent extraction procedure, Fe(III) could be efficiently recovered by using 0.1 mol/L bis(2-ethlhexyl) phosphate (D2EHPA) at pH 1.5 with an Aqueous/Organic ratio of 1 over 10 min. The results indicated that the extraction percentage of Fe(III) was beyond 99%. Eventually, the recoveries of nickel and chromium were respectively 99.5% and 75% through chemical precipitation.

Keywords: stainless steel sludge; hydrometallurgy; D2EHPA; solvent extraction; chemical precipitation

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1. Introduction

Recently, steel has been the widest applied material among diverse metals due to the rapid development of technology [1]. Nevertheless, the quality of stainless steel in appearance and corrosion resistance are more exceptional, which makes it pervasive in modern society. According to the International Stainless Steel Forum (ISSF) report, stainless steel consumption was primarily used for metal products and mechanical engineering in 2021. Furthermore, ISSF also forecast that the global demand for stainless steel will increase in the future, so the treatment of the wastes such as slag [2] and sludge [3,4] is a critical issue. Stainless steel sludge was generated during the operation of large-scale machinery for the manufacturing industries. The solidified landfill is the most common waste treatment method. However, the leakage of the heavy metals not only results in environmental disruption but also harm to animals [5,6]. Especially for Cr(III), the conversion of Cr(III) to Cr(VI) is fatal to human beings as Cr(VI) causes health effects on the respiratory system, immune system, liver, and kidney [7,8]. Consequently, hydrometallurgy techniques have been developed to deal with the waste, such as solvent extraction, ion exchange, chemical precipitation [9–11], and electrochemistry [12], making the procedure more environmentally friendly.

In order to recover the valuable metals from stainless steel sludge, the hydrometallurgical method was applied in this study due to its high efficiency, low energy consumption, and easy implementation. The operations including acid leaching, solvent extraction, and chemical precipitation were carried out to separate the valuable metals. In hydrometallurgical procedures, employing an inorganic acid as a lixiviating agent such as HCl [13], H_2SO_4 [14], or HNO_3 [15] is the most common method. According to those given in the literature, HCl, H_2SO_4, and HNO_3 can efficiently dissolve the metals out of stainless steel. Hence, this research focused on investigating the leaching ability of these acids and choosing a suitable lixiviating agent.

Because the chemicals perform different extraction behaviors under various conditions, several extractants, resins [16,17], and precipitating agents were applied to dispose of the wastes in the separation procedure, such as Cyanex 272/Cyanex 301/Cyanex302 [18–22], LIX984N-C [23], LIX 54 [24], TEA [25], and D2EHPA [26–29]. Sole et al. [30] used Cyanex 272, Cyanex 301, and Cyanex 302 to investigate the extraction efficiency of the metal ions under diverse pH conditions. Nonetheless, based on the literature, the pH values of the best extraction efficiency for Ni(II) and Cr(III) are beyond 2.0, which leads to the precipitation of Fe(III) and co-precipitation. Therefore, it is necessary that Fe(III) should be removed at first before separating nickel and chromium. Hu et al. [31] used D2EHPA to extract Fe(III) from the leaching solution, and the results indicated that D2EHPA has an excellent extraction efficiency and selectivity of Fe(III) over other metal ions. In addition, according to the Pourbaix diagram [32], Ni(II) can be separated from Cr(III) by adjusting oxidation-reduction potential (ORP) and pH value. Although it is a simple way to cope with the sludge, the generation of Cr(VI) still needs to be considered. The conventional method for Cr(VI) removal is to reduce Cr(III) at pH 2.0 and precipitation of $CrOH_3$ with lime at pH 9–10 [33]. Dettmer et al. [34] used sodium sulfite to reduce hexavalent chromium of the leather wastes at pH 2.0 and produced the basic sulfate chromium which had similar basicity properties compared with the commercial product.

Apart from hydrometallurgical methods, pyrometallurgy treatment was also employed to address the stainless steel sludge and dust. Liu et al. [35] recovered iron, chromium, and nickel from stainless steel dust and reached the goals of high metal recoveries through direct reduction and self-pulverization separation. The recoveries of the three metals were respectively 92.50%, 92.02%, and 93.74%. Tang et al. [4] utilized a coal-based smelting reduction process to deal with pickling sludge. The metals in the sludge were recovered in the form of Fe-Cr-Ni-C alloys. Although pyrometallurgy treatment was simple and straightforward, the procedure at high temperature (>1000 °C) would result in high energy consumption. Therefore, hydrometallurgy was adopted as the primary technique in this wok to attain high metal recoveries and purities, which makes the metal products have various applications.

In this study, the oil and water content of stainless steel sludge has been removed by pre-treatment procedures. Afterwards, HCl, H_2SO_4, and HNO_3 were employed to leach the remaining solids, and the leaching percentages were also examined. Solvent extraction of Fe(III) was conducted through D2EHPA as an extractant. Moreover, to optimize the extraction efficiency, the influences of the pH value, extractant concentration, aqueous-organic ratio, and reaction time were also investigated. Lastly, chemical precipitation was applied to separate nickel and chromium according to the Eh-pH diagrams. To sum up, this research aimed to design an improved recovery system and combine the advantages of leaching, solvent extraction, and chemical precipitation mentioned above to achieve effective results.

2. Materials and Methods

2.1. Materials, Reagents, and Instruments

In this research, the sludge which had been the accumulation of stainless steel scraps with lubricant was collected from the local recycling center for the use of the experiment. In the pre-treatment procedure, oil and water were removed by a muffle furnace (LE 6/11, Naberthem, Li-lienthal, Germany), and the residue would be ground by a ball mill at 260 rpm for 24 h and sieved with a 100-mesh screen to increase the leaching percentages of iron, nickel, and chromium. The sulfuric acid (H_2SO_4, 98%, Sigma-Aldrich, St. Louis, MI, USA), hydrochloric acid (HCl, 36.5%, Sigma-Aldrich, USA), and nitric acid (HNO_3, 65%, Sigma-Aldrich, USA) were used as leaching agents and diluted in deionized water. Sodium hydroxide (NaOH, 97%, SHOWA, Gyoda, Japan) and hydrochloric acid were employed to adjust the pH value. Bis(2-ethlhexyl) phosphate (D2EHPA, 95%, Alfa Aesar, Haverhill, MA, USA) diluted into kerosene was used as an extractant to separate Fe(III) from the leach liquor. Hydrogen peroxide (H_2O_2, 36.5%, Sigma-Aldrich, USA) and sodium hydroxide were applied to adjust the oxidation-reduction potential (ORP) and the pH value in chemical precipitation according to the Pourbaix diagram. Sodium sulfite (Na_2SO_3, 100%, Honeywell, Charlotte, NC, USA) was utilized as a reductant of chromate ions. Chemical reagents used in the experiment were all analytical grades.

2.2. Pre-Treatment

The stainless steel sludge is mainly composed of oil, water, and ash. The proportions analysis by weight of the components were observed and determined by Differential Thermal Analysis/Thermogravimetry Analysis (DTA/TG, NETZSCH-409PC, Netzsh, Selb, Germany). After the sludge was calcined by a muffle furnace, the remaining solids were ground into powder and sieved with a 100-mesh screen. The crystal structure analysis was analyzed by X-ray Diffraction Meter (XRD, Dandong DX-2700, Dandong Kemait Ndt Co., Ltd., Dandong, China). The metal concentrations for separation and leaching efficiencies were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian, Vista-MPX, Palo Alto, CA, USA).

2.3. Acid Leaching

Leaching procedures were conducted applying standard laboratory leaching equipment. The powder of the residue was dissolved in 4 mol/L HCl, HNO_3, and H_2SO_4 to investigate the leaching efficiency and select the lixiviating agent. To achieve a better leaching percentage, the effect of calcination temperature was also studied and tested at 300 °C, 600 °C and 900 °C for 8 h. The leaching efficiency was calculated according to Equation (1):

$$X_B = \left(\frac{m_1}{m_1+m_2}\right) \times 100\% \tag{1}$$

where X_B is the leaching efficiency, m_1 is the measured quantity of metal leached, and m_2 is the quantity of metal in remaining solids.

2.4. Solvent Extraction

In this study, D2EHPA was used to efficiently extract Fe(III) from the leach liquor. The extractant was first diluted into kerosene and was then thoroughly mixed with the leaching solution for extraction. The extraction mechanism of D2EHPA can be written as Equation (2) [26]:

$$Fe^{3+} + 3H_2A_{2(org)} \rightarrow Fe(HA_2)_{3(org)} + 3H^+ \tag{2}$$

The distribution ratio, D, is the concentration ratio of the metal in the organic phase to that in the aqueous phase at equilibrium. Hence, the distribution ratio can be written as Equation (3):

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{C_i - C_f}{C_f} \tag{3}$$

where $[M]_{org}$ and $[M]_{aq}$ are the metal concentrations in the organic and aqueous phases. C_i is the initial concentration of metal ions in the aqueous phase and C_f is the equilibrium concentration of metal ions in the aqueous phase.

From the distribution ratio, D, the extraction percentage, %E can be calculated by Equation (4):

$$\%E = \frac{D}{D + V_{aq}/V_{org}} \times 100\% \tag{4}$$

where D is the distribution ratio. V_{aq} and V_{org} are the volumes of the aqueous phase and organic phase.

The separation factor, β, defines the selectivity for target metal (M_A) over another metal (M_B). From the distribution ratios of two metals, the separation factor, β can be calculated by Equation (5):

$$\beta_{A/B} = \frac{D_A}{D_B} = \frac{[M_A]_{org} \times [M_B]_{aq}}{[M_B]_{org} \times [M_A]_{aq}} \tag{5}$$

where D_A and D_B are the distribution ratio of target metal and the others. $[M_A]_{org}$ and $[M_B]_{org}$ are the metal concentrations in the organic phase after solvent extraction. $[M_A]_{aq}$ and $[M_B]_{aq}$ are the metal concentrations in the aqueous phase after solvent extraction.

2.5. Chemical Precipitation

According to the Pourbaix diagram of nickel and chromium, NaOH and H_2O_2 were applied as the reagent to separate these two metals in the chemical precipitation process. The following chemical equations illustrate the separation and precipitation of Ni(II) and Cr(III) [34]:

$$Ni^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightarrow Ni(OH)_{2(s)} \tag{6}$$

$$2Cr^{3+}{}_{(aq)} + 3H_2O_{2(aq)} + 10OH^{-}{}_{(aq)} \rightarrow 2CrO_4{}^{2-}{}_{(aq)} + 8H_2O_{(l)} \tag{7}$$

$$CrO_4{}^{2-}{}_{(aq)} + 2H^{+}{}_{(aq)} + 3SO_3{}^{2-}{}_{(aq)} \rightarrow Cr^{3+}{}_{(aq)} + H_2O_{(l)} + 3SO_4{}^{2-}{}_{(aq)} \tag{8}$$

$$Cr^{3+}{}_{(aq)} + 3OH^{-}{}_{(aq)} \rightarrow Cr(OH)_{3(s)} \tag{9}$$

The precipitation percentage is calculated by Equation (10):

$$P = \frac{[M]_0 \times V_0 - [M] \times V}{[M]_0 \times V_0} \times 100\% = 1 - \frac{[M] \times V}{[M]_0 \times V_0} \times 100\% \tag{10}$$

where P is the precipitation percentage, $[M]_0$ is the metal concentration of the leach liquor, and $[M]$ is the metal concentration of the leach liquor after precipitation. V_0 and V were the volumes of the solution before and after chemical precipitation, respectively. The whole procedure of the experiment is shown in Figure 1.

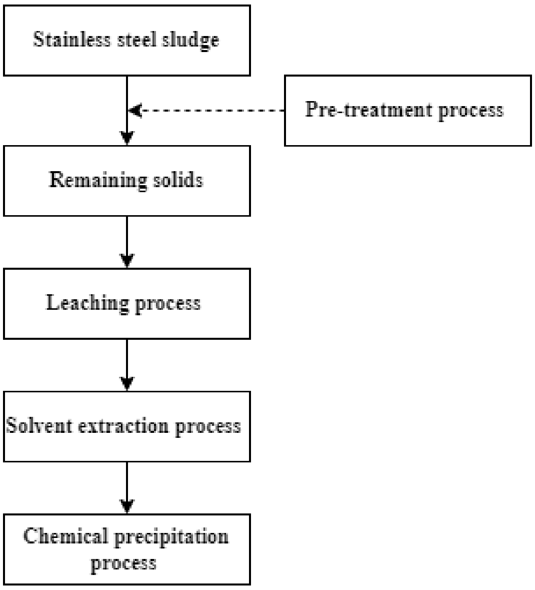


Figure 1. The outline of recovery system for iron, nickel, and chromium from stainless steel sludge.

3. Results and Discussion

3.1. Pre-Treatment

The thermogravimetric analysis of stainless steel sludge is shown in Figure 2 to observe the mass change with temperature. There was a rapid and tremendous mass change between 200–300 °C, and the mass loss in the temperature interval was the combustion of the organic compound. After 300 °C, the mass gradually increased with temperature due to metal oxidation. The proportion by weight is shown in Table 1, illustrating that the oil, water, and ash content accounted for 37–39%, 1–3%, and 58–62%, respectively. Table 2 shows the concentration of iron, nickel, and chromium analysis by ICP-OES after pre-treatment (heat at 900 °C). It could be found that iron is the dominant element compared to nickel and chromium in stainless steel sludge. On the basis of the results, the concentration of these three metals of the sludge has the economic value to recycle. The hydrometallurgical methods were applied to separate iron, nickel, and chromium in this research.

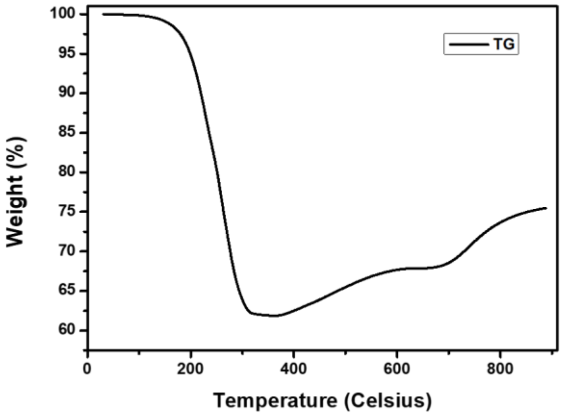


Figure 2. Thermogravimetric analysis of stainless steel sludge.

Table 1. Proportions of stainless steel sludge by weight.

Composition	Oil	Water	Ash
Proportion (wt%)	37–39	1–3	58–62

Table 2. The metal concentrations of stainless steel sludge after pre-treatment.

Element	Fe	Ni	Cr
Concentration (mg/L)	2380	300	307

3.2. Acid Leaching

After removing oil and water content, the remaining solids were ground and then sieved with a 100-mesh screen to increase contacting area and leaching efficiency. The metal concentrations of sludge after pre-treatment are shown in Table 2. The sludge calcined at 900 °C for 8 h was leached by 4 mol/L HCl, H_2SO_4, and HNO_3 with liquid-solid mass ratio of 100 mL/g, 24 h, and 25 °C. The result in Figure 3 indicates that HCl had the highest leaching efficiency for iron, nickel, and chromium. Due to the existence of Cl^-, it caused pitting corrosion to enhance the ability of acid leaching while the effects of HNO_3 and H_2SO_4 were not significant [36]. Therefore, 4 mol/L HCl was chosen for the leaching process.

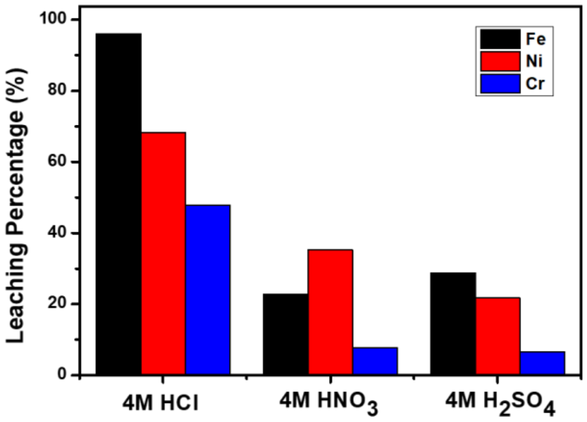


Figure 3. The effect of acids on the leaching percentage.

As the leaching percentage did not reach the ideal condition, this research investigated the calcination temperature which was carried out to improve the efficiency. According to Table 3, sludge calcined at 300 °C had the best leaching percentage. However, the efficiency decreased when the temperature reached 600 °C. Figure 4 shows the XRD analysis of the sludge calcined at 600 °C. It could be found that the remaining solid was mainly composed of Fe_2O_3 and Fe_3O_4, which greatly prevented the metal from dissolving and lowered the leaching rate. According to the literature [37], the thickness of the oxide layer increased with the temperature. The results also correspond with the TG analysis that the mass increased with temperature due to metal oxidation after 400 °C. Hence, 300 °C was chosen for the optimal calcination temperature. To sum up, it was determined as the optimal condition that sludge calcined at 300 °C was leached by 4 mol/L HCl, liquid-solid mass ratio of 100, 24 h, and 25 °C, and the leaching efficiency of iron, nickel, and chromium were respectively 97.6%, 98.1%, and 95.7%.

Table 3. The effect of calcination temperature on the leaching percentage.

Element	Fe	Ni	Cr
300 °C	97.6%	98.1%	95.7%
600 °C	40.3%	32.7%	12.8%

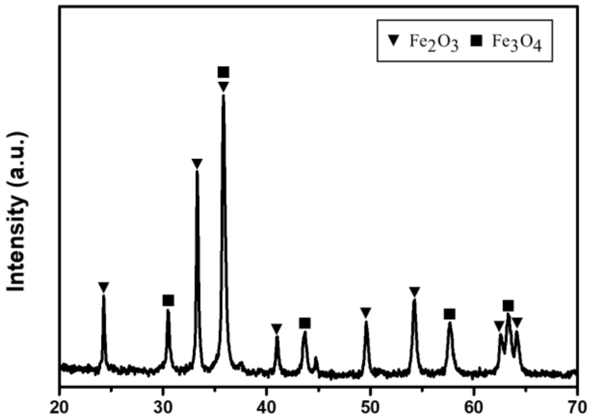


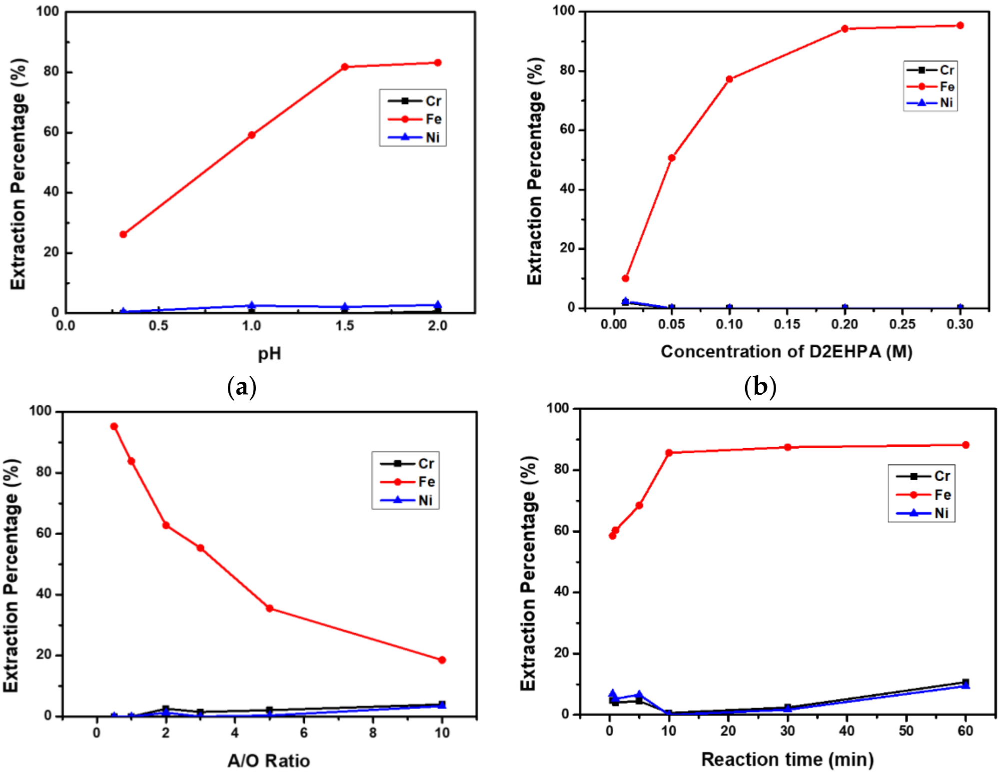
Figure 4. The X-ray diffraction (XRD) pattern of stainless steel sludge calcined at 600 °C.

3.3. Solvent Extraction with D2EHPA

Since stainless steel sludge contains an extremely high proportion of iron, D2EHPA was used first to separate it from the leach liquor. If the iron was not separated first, it would have a negative impact such as co-precipitation due to the relatively small amount of nickel and chromium. Therefore, we applied D2EHPA to solve the problem in this research. The concentration ratio of iron, nickel, and chromium was set 2323:294:294 mg/L which was according to the leaching results. After solvent extraction, the metal concentrations were analyzed by ICP-OES to calculate the extraction efficiencies.

3.3.1. Effect of pH Value of the Aqueous Phase

The extraction pH value was regarded as the most influential factor due to the different extraction behavior of extractants in a wide range of pH values. D2EHPA was employed to effectively extract Fe(III) ions from the acidic solution. However, Fe(III) ions precipitated with nickel and chromium while the pH value was beyond 2.0. To investigate the effect of extraction behavior of Fe(III) through D2EHPA, the pH values were set up from 0.3 to 2.0 by using 0.1 mol/L D2EHPA with an aqueous-organic ratio of 1:1 over 30 min. Figure 5a reveals that the extraction percentage of Fe(III) increased from 26.1% to 83.2% with the raising pH value. According to Equation (2), the chemical reaction proceeded to the right when the concentration of H^+ decreased, which led to a higher extraction efficiency. Hence, the optimal pH value was chosen as pH 1.5 in this step.



(**a**) (**b**)

(**c**) (**d**)

Figure 5. (**a**) Effect of the extraction percentage on pH value. (**b**) Effect of the extraction percentage on D2EHPA concentration. (**c**) Effect of the extraction percentage on aqueous-organic ratio. (**d**) Effect of the extraction percentage on reaction time.

3.3.2. Effect of D2EHPA Concentration

In this procedure, the extraction of Fe(III), Ni(III), and Cr(III) was investigated with conditions of D2EHPA concentration from 0.01 to 0.3 mol/L at pH 1.5 and an aqueous-organic ratio of 1:1 over 30 min. Figure 5b shows that the extraction percentage of Fe(III) rose rapidly with increasing D2EHPA concentration from 0.01 to 0.2 mol/L. This means that the higher the concentration of extractant, the more Fe(III) ions there are to be caught. Although the extraction efficiency reached up to 95% at a concentration above 0.2 mol/L, 0.1 mol/L was chosen as the optimal parameter to be cost-effective.

3.3.3. Effect of A/O Ratio

A/O ratio refers to the amount of aqueous phase (leach liquor) to the amount of organic phase (extractant). Figure 5c illustrates that the A/O ratios were set from 0.5 to 10 with the fixed parameters of pH 1.5 and D2EHPA concentration of 0.1 mol/L over 30 min. The result reveals that the extraction efficiency of Fe(III) decreased as the A/O ratio increased. The reason was that the extractant was insufficient to extract the Fe(III) ions. Therefore, Aqueous-organic ratio of 1:1 was the optimal parameter in this process.

3.3.4. Effect of Reaction Time

In Figure 5d, the reaction periods were set from 0.5 to 60 min, which was studied by using 0.1 mol/L D2EHPA at pH 1.5 and the aqueous–organic ratio was 1. The result indicates that D2EHPA had an incomplete reaction with Fe(III) from 0.5 to 5 min since it still had selectivity of nickel and chromium. The extraction of Fe(III) reached 80% and tended to be equilibrium after 10 min. On the other hand, the extraction percentage of nickel and chromium began to increase as well. To avoid the co-extraction problem of these two metals, a reaction time of 10 min was chosen in this research.

Table 4 displays the distribution ratios and the separation factors of the metals. It could be found that 0.1 mol/L D2EHPA has a high selectivity for Fe(III) at pH 1.5 with an A/O ratio of 1 and contacting time of 10 min.

Table 4. Distribution ratios and separation factors of iron, nickel, and chromium after 0.1 mol/L D2EHPA solvent extraction at pH 1.5 with an A/O ratio of 1 and contacting time of 10 min.

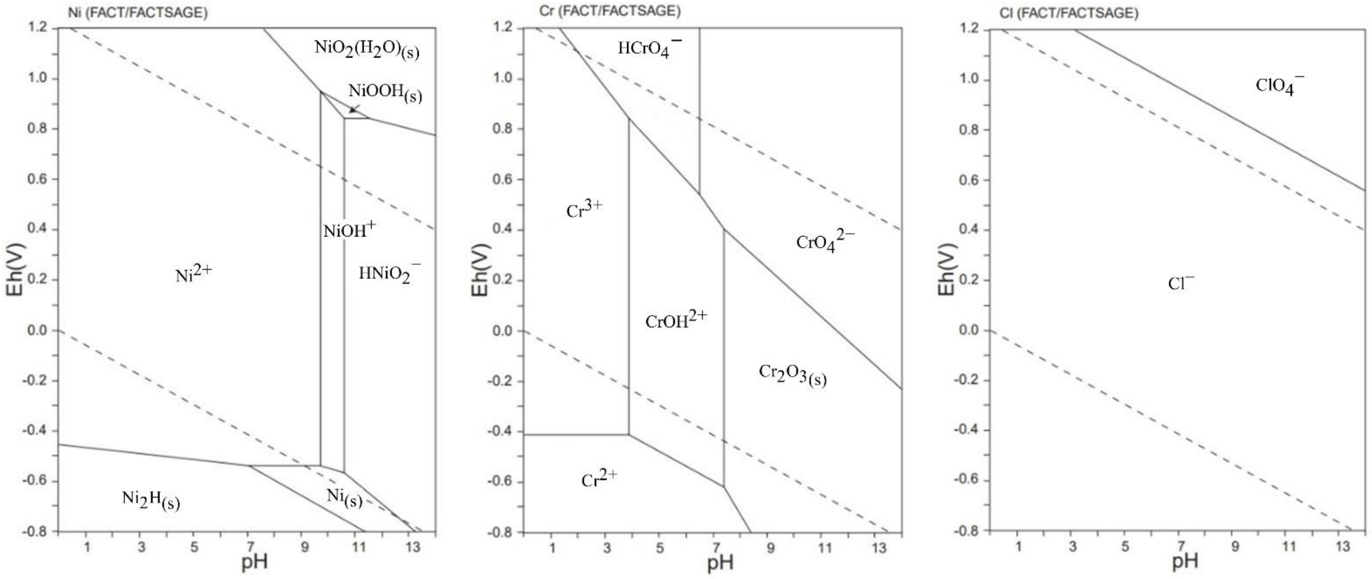
Distribution Ratios		Separation Factors	
D_{Fe}	5.98	$\beta_{Fe/Ni}$	1616.22
D_{Ni}	0.0037	$\beta_{Fe/Cr}$	906.06
D_{Cr}	0.0066		

3.4. Chemical Precipitation with NaOH

After the two-stage solvent extraction of Fe(III) from the leach liquor, chemical precipitation was carried out to separate nickel and chromium. Table 5 shows the metal concentrations of the raffinate after Fe(III) removal. According to the Pourbaix diagrams in Figure 6, it could be found that Cr(III) was oxidized as CrO_4^{2-} by raising the oxidation-reduction potential (ORP) above −200 mV at pH 14. Meanwhile, nickel precipitated as nickel hydroxide could be recycled. In this study, the pH and the ORP were adjusted by applying the saturated sodium hydroxide solution and hydrogen peroxide solution, respectively. The results reveal that the precipitation percentage of nickel was above 99% whereas the recovery rate of CrO_4^{2-} was approximately 75%. To increase the purity of nickel hydroxide and the recovery rate of CrO_4^{2-}, hot water was used to wash out the remaining CrO_4^{2-}. Moreover, the reduction of CrO_4^{2-} was conducted by utilizing sodium sulfite at pH 2.0 due to its high toxicity, and then the Cr(III) precipitated as $Cr(OH)_3$ at pH 10. The comparisons between the results of this study and others are shown in Table 6. It demonstrates that the recovery efficiencies of iron and nickel in this work were higher than in other recycling methods. Nevertheless, the recovery rate of chromium was lower, which can be enhanced by rinsing with hot water after the precipitation of nickel.

Table 5. The metal concentrations of the raffinate.

Element	Fe	Ni	Cr
Concentration (mg/L)	0.004	293	292



(**a**) (**b**) (**c**)

Figure 6. The Eh-pH diagrams of (**a**) nickel, (**b**) chromium, and (**c**) chlorine.

Table 6. The recovery rates of metals from stainless steel waste by different recycling technologies.

References	Materials	Recycling Technologies	Recovery Rate
Zhang et al. [38]	Pickling sludge	Reduction and magnetic separation	Fe 70.1%, Ni 60.3%, Cr 53.7%
Liu et al. [39]	Stainless steel dust	Carbon-thermal reduction	Fe 79.7%, Ni 83.6%, Cr 90.7%
Wu et al. [5]	Pickling sludge	Direct reduction and magnetic separation	Fe 95.3%, Ni 97.5%, Cr 88.7%
This study	Stainless steel sludge	Solvent extraction and chemical precipitation	Fe 99.9%, Ni 99.5%, Cr 75.1%

4. Conclusions

This research investigated the purpose of recycling iron, nickel, and chromium from stainless steel sludge through hydrometallurgical methods, namely acid leaching, solvent extraction, and chemical precipitation. The leaching efficiencies of iron, nickel, and chromium were respectively 97.6%, 98.1%, and 95.7% by applying 4 mol/L HCl to lixiviate the sludge calcined at 300 °C. Furthermore, this study was dedicated to maximizing the efficiency of recovery and separation through solvent extraction. The results indicated that 0.1 mol/L D2EHPA could efficiently extract 80% of Fe(III) at pH 1.5 with an A/O ratio of 1 and contacting time of 10 min. The separation factors for Fe/Ni and Fe/Cr were 1616.22 and 906.06, respectively. To reach a higher extraction efficiency, this study carried out a two-stage extraction to achieve over 99% of the extraction percentage. Finally, the separation of nickel and chromium was conducted according to the Pourbaix diagram. The recovery rates were 99.5% and 75%, respectively. In addition, sodium sulfite was used to reduce CrO_4^{2-}, and then the Cr(III) precipitated as $Cr(OH)_3$ at pH 10. In this way, the metal products recovered from the stainless sludge can be reused in the industries to decrease the waste and reach the goal of resource recycling. However, there are still some improvements needed in this recovery system. For instance, the oil in the sludge could also be recycled to reduce the emission of carbon dioxide during calcination, and the parameters of leaching and stripping should be investigated further to increase the application potential.

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Y.-C.C.; writing—review and editing, Y.-C.C. and C.-H.L. All authors have read and agreed to the published version of the manuscript.

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