



Selective Separation of Iron and Cobalt from Leached Tungsten Carbide Scrap by Solvent Extraction

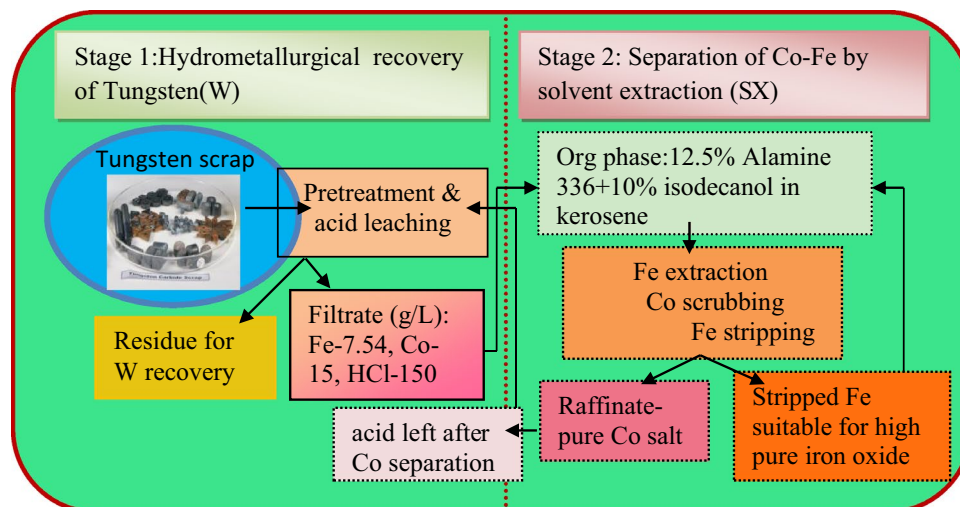
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Abstract

Chloride leaching of the oxidized tungsten carbide scrap generated a leach liquor of composition(g/L): Fe-7.54, Co-15 & HCl-150, which was used to investigate the selective separation of iron and cobalt by its liquid–liquid interaction with 12.5%(v/v) Alamine-336 + 10%(v/v)isodecanol in kerosene. Effect of various parameters such as solution acidity, solvent concentration, phase modifier concentration, iron and cobalt concentration(externally) in the feed solution, were optimized. McCabe–Thiele plots for maximum Fe extraction and stripping were made to decide the number of stages at desired O/A ratio. The pure iron and cobalt solutions obtained can be used to synthesize desired product. Remaining acid and regenerated solvent could be recycled to the leaching tank and re-extraction. The overall process has been attempted to function in a close-loop mode.

Graphical Abstract



Keywords WC-scrap · Solvent extraction · Alamine-336 · Fe–Co separation · FTIR

Introduction

Tungsten(W) is a strategic metal important for economic development and national security. Due to its limited and highly localized global deposits, recovery from secondary sources has increased significantly. More than 60% of tungsten is consumed in the manufacturing of tungsten carbide(WC)-based hard metal tools [1], which is the single

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largest secondary source of tungsten (> 80%), Co (5%) and Fe (2%). The commercial processes for WC scraps recycling focus only on the recovery of tungsten values and rejecting the coexisting Co and Fe [2]. This work deals with the reclamation of metal values from WC scrap in light of the economic, environmental and ecological factors. Cobalt is a strategic metal and its recovery from these scraps will enhance the process economy and value addition [3]. Hydro-metallurgical [4–6] treatment of these wastes can recover all the metal constituents in the pure form. Acid leaching of the WC scrap generates a highly acidic filtrate containing Co and Fe with the recovery of tungsten as residue. Separation and recovery of pure Co and Fe from this filtrate is the aim of this work. Fe containing acidic wastes are generally neutralized to precipitate metal hydroxide but the precipitate filtration is the major disadvantage. To overcome these problems solvent extraction is a simple, rapid and economical option for the selective extraction and separation of metal values.

Since the Concentration of Co was Very High it was Decided to Extract Fe Selectively

A brief overview on the solvent extraction of Fe from acid chloride solutions is given below. Formation of strong complexes of Fe(III) with Cl^- in the aqueous phase [7–9] affects the extraction and stripping characteristics of the system. Fe(III) from chloride solutions was extracted using anionic solvent such as amines and quaternary ammonium salts. Solvents containing carbonyl/polyether group gave promising results but dissolve beyond 6 N HCl [10]. Extraction of Fe(III) ions from HCl solutions were attempted using tri-*n*-octylamine and Aliquat-336 [11], methyl isobutyl ketone extraction (MIBK) and acetophenone [12], tri butyl phosphate [13], tributyl phosphate + methyl isobutyl ketone extraction in kerosene [14], di-(2-ethylhexyl) phosphoric acid [15], Alamine 336 [16]. Zhou et al. [17] eliminated a third phase formed using oxygen-containing organic compound, during the extraction of Fe(III)/Co(II) with a tertiary amine. Various Fe complexes such as R_4NFeCl_4 [18], $\text{FeCl}_3 \cdot 3\text{TBP}$ and $\text{HFeCl}_4 \cdot 2\text{TBP}$ [19], HFeCl_4 [20] were reported during the extraction of Fe with amine and neutral solvents. Synergistic effect was observed on Fe(III) extraction using methyl isobutyl ketone, tri butyl phosphate, di-(2-ethylhexyl) phosphoric acid and their mixtures [21, 22]. Recently ionic liquids were used to extract Fe and Mn from aqueous solution [23].

Based on the leach liquor composition the concentration of Co was much higher than that of Fe, hence it was decided to extract Fe selectively with cobalt remaining unextracted in the raffinate in a pure form. Therefore, the extraction of cobalt was not attempted. Co recovery from the acidic raffinate will be done systematically in the next step either by cementation [24] crystallization or by solvent extraction [25–27].

Of the various solvents such as methyl isobutyl ketone, tri butyl phosphate, mixture of di-(2-ethylhexyl) phosphoric acid

and methyl isobutyl ketone, tried for Fe(III) extraction from this leach liquor, Alamine-336 was selected for this work due to several advantages such as: fast and clear phase separation, water insoluble, presence of the basic nitrogen atom which reacts with a variety of inorganic and organic acid forming oil soluble anionic salts at low pH. This solvent can be stripped with a wide variety of inorganic salt solution which decides the overall recovery of the extracted metal. A detailed discussion on the experimental parameters optimized for the separation of Fe(III) and Co present in the leach liquor is given below.

Experimental

Alamine-336, supplied by Henkel (Germany) was used as procured. Distilled kerosene (150–275 °C fraction) and isodecanol were used as diluent and phase modifier. Physico-chemical properties of the extractant, phase modifier and diluent are summarized in Table 1. All other chemicals used were of AR grade supplied by BDH/Merck. Tungsten scrap was collected from a company at Mangalore, India. The leach liquor generated after tungsten recovery was used in the solvent extraction study for the separation of Fe and Co along with the acid.

Extraction Procedure

Working Leach liquor (WLL) contained (g/L): Fe-7.54, Co-15, HCl-4 M (150 g/L). Equal volume (10 mL) of aqueous and organic phases (unless otherwise stated) were mixed in a separatory funnel for a desired time by shaking in a wrist action shaker. After phase disengagement the aqueous phase was tapped out for analysis. Various parameters were studied to optimize the best experimental conditions. Concentration and volume of isodecanol (phase modifier) and Alamine-336 were optimized for the maximum extraction efficiency for Fe(III). Effect of varying concentration of Co, Fe(III), acid and chloride were studied to find out the extent of co-extraction of Co during Fe(III) extraction. Under the optimized condition the iron-loaded organic was generated to study the scrubbing of the co-extracted Co and stripping of iron. All the experiments were performed in triplicate to ensure the reproducibility of the extraction. Since the aqueous solubility of isodecanol, Alamine-336 and kerosene were negligible (Table 1), the organic concentration was assumed to remain unchanged during the extraction and was verified experimentally.

Treatment of Extraction Data and Analytical Procedure

The high Fe(III) concentration in the solution was determined by dichromate titration using Barium diphenyl-sulphonate indicator [28]. Low concentration of Fe(III) and Co

Table 1 Physical and chemical properties of solvent, phase modifier and diluent used in this work

Sl No	Property	Properties of each component in the solvent mixture		
		Extractant	Phase Modifier	Diluent
		Alamine 336	Iso decanol	Kerosene
1	Chemical formula	Tertiary amine content 95–100%, Secondary amine content < 5.0% $C_{24}H_{51}NR_3N$ (R: C_8 – C_{10})	Mixt of $C_{10}H_{21}OH$ isomer $C_{10}H_{22}O$	C chains containing C between 6 and 16 atoms/molecule. It's a distillation fraction between 150 and 275 °C
2	Flash point	179 °C	104 °C	37–65 °C
3	Melting point	– 34 °C	6.4 °C	– 45.6 °C
4	Auto ignition temp	–	226 °C	220 °C
5	Boiling point	164–168 °C	215–225 °C	150–300 °C
6	Mol. Wt.	353.67 g/mol	158.3 g/mol	No data
7	Color(APHA)	< 500	APHA 10 max	Pale yellow
8	Sp gravity g/cm ³	0.81	0.836–0.842	0.78–0.81
9	Clarity	Clear	Clear liquid	Clear
10	Pour point	– 54 °C	– 54 °C	37–65 °C
11	Surface tension (dynes/cm at 25 °C)	34.8	8.97	23–32
12	Viscosity(N s/m ² , Pas at – 34.6 °C)	7.86×10^{-2}	0.001204	0.00164
13	Solubility	Acetone-13 Water < 5 ppm Completely Miscible in: C_6H_6 , CCl_4 , $CHCl_3$, Ethanol, cyclohexane, Di-iso butyl ketone, isopropanol, <i>kerosene</i> , n butanol, <i>n decanol</i>	Immiscible in water	Immiscible in water

were analyzed by Atomic Absorption Spectrophotometer (SOLAAR-S2). Fe(III) concentration in the organic phases was calculated by mass balance i.e. the difference of Fe concentration before and after extraction in the raffinate.

The distribution coefficient (D_{Fe}) is the ratio of the concentration of Fe(III) ion in the organic and aqueous phase at equilibrium.

Thus

$$D_{Fe} = \frac{[Fe(III)]_{org.eq} \cdot V_{aq}}{[Fe(III)]_{aq.eq} \cdot V_{org}} \quad (1)$$

And $[Fe(III)]_{org.eq} = [Fe(III)]_{aq,total} - [Fe(III)]_{aq.eq}$.

The percentage extraction (%E) of Fe(III) was given by

$$\%Extraction = 100 \times \frac{[Fe(III)]_{org.eq}}{[Fe(III)]_{aq,total}} = 100 \times \frac{[Fe(III)]_{aq,total} - [Fe(III)]_{aq.eq}}{[Fe(III)]_{aq,total}} \quad (2)$$

$[Fe(III)]_{aq,total}$, $[Fe(III)]_{org.eq}$ & $[Fe(III)]_{aq.eq}$ represents the initial Fe(III) concentration, Fe(III) extracted by the solvent and left un-extracted in raffinate at equilibrium.

V_{aq} & V_{org} = Vol of the aqueous and organic phases taken during extraction.

Distilled water at pH 3 was used to strip Fe(III) from the loaded organic. An equal volume of Fe(III) loaded organic and the stripping agent was mixed in a separatory funnel for 5 min. Aqueous phase was tapped out and analyzed for Fe(III) stripped. The percent Fe(III) stripped was calculated as:

$$\%Stripping = \frac{[Fe(III)]_{aq,stripped}}{[Fe(III)]_{loaded.org}} \times 100 \quad (3)$$

$[\text{Fe(III)}]_{\text{loaded.org}} + [\text{Fe(III)}]_{\text{aq.stripped}}$ = amount of Fe(III) present in the loaded organic & Fe(III) stripped.

Results and Discussion

WLL (filtrate) obtained after tungsten recovery containing appreciable amount of Fe and Co was subjected to solvent extraction to separate Fe and Co, using Alamine-336. Experimental conditions were optimized to extract maximum amount of Fe(III) from WLL.

Equilibrium Time

WLL was contacted with 12.5% (v/v or 0.25 M) Alamine-336 + 10% isodecanol + kerosene for a time ranging from 1 to 10 min at O/A:1. The equilibrium attained in 5 min was maintained in all the experiments.

Effect of Alamine-336 Concentration

Alamine-336 concentration was varied from 0.05 to 0.46 M in kerosene + 10% isodecanol at O/A-1 and time-5 min. The result (Fig. 1a) shows that Fe extraction increases rapidly at lower solvent concentration and becomes gradual as the concentration increases.

87% Fe(III) and 0.2% Co was extracted with 0.25 M (12.5% v/v) of Alamine-336, which was used in all the further experiments. Plot of $\log D_{\text{Fe}}$ vs. $\log[\text{Alamine-336}]$ (Fig. 1b) shows a deviation from linearity within the concentration range tested. Two regions of linearity with a slope of 1.38 and 3.21 in the concentration range from 0.05 to 0.23 M and 0.23–0.46 M, respectively, were obtained indicating the association of 1 and 3 mol of the extractant with one mole of iron. Good and Srivastava [29] reported the possibility of polymerization of amine solvent beyond dimer at 0.05 M and above.

Effect of Phase Modifier

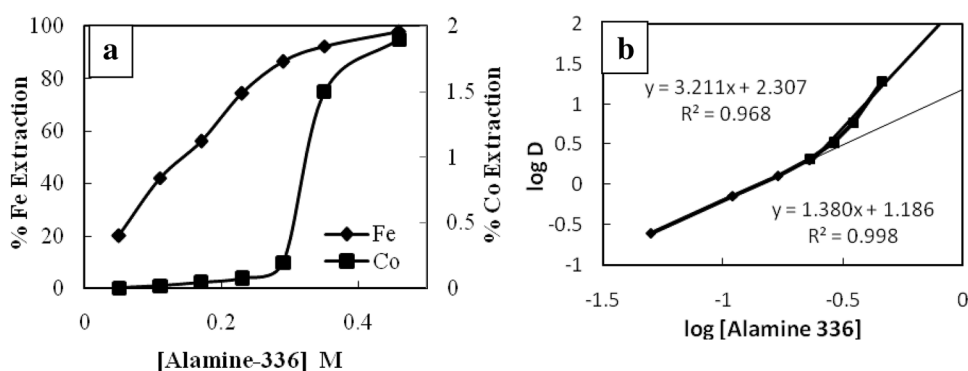
A third phase was observed on the extraction of Fe(III) from WLL using 12.5% Alamine-336 + kerosene (no phase modifier), affecting the performance of the organic solvent.

Adding 10 mL of various phase modifiers such as tri butyl phosphate, methyl isobutyl ketone, octanol and nonylphenol, only isodecanol was found to be most suitable for this system due to clear and fast phase separation and was used in all the further investigations. Isodecanol was varied from 1 to 40% (V/V) to optimize its desired concentration in the present work. Figure 2a indicates the disappearance of the third phase with the increase in isodecanol concentration from 5% and above, with a marginal increase in Fe extraction beyond 10% isodecanol. Hence 10% isodecanol was sufficient to give a clear loaded organic. A gradual disappearance of the third phase with the increase in isodecanol concentration was substantiated by FTIR (ALPHA FTIR Spectrometer, Bruker) (Fig. 2b–d) analysis of the Fe(III) loaded organic and the third phase at different modifier concentration. IR data of organic and third phase on isodecanol variation are given in Fig. 2e. In IR spectrum (Fig. 2b), peaks at 879.33 cm^{-1} and 1048 cm^{-1} were due to third phase formation when 0–3% isodecanol was added to 12.5% Alamine-336 + kerosene. The peak at 879.33 cm^{-1} may be assigned to the presence of asymmetric Fe–O stretching band and at 1048 cm^{-1} was assigned to the stretching frequency of C–O for isodecanol [30]. With further increase in isodecanol, these peaks gradually merge into the organic layer (1048 cm^{-1}), which finally disappeared on increasing the isodecanol concentration up to 30%. Thus, 10% isodecanol was optimized for further experiments due to its ability to arrest third phase formation.

Effect of H^+ and Cl^- Concentration

The extraction of Fe(III) from WLL increased with the increase in $[\text{HCl}]$ from 0.5 to 8 M. Below 0.3 M HCl a third layer (yellowish gel) was observed and phase separation was not possible. The individual effect of H^+ concentration on Fe(III)/Co(II) extraction was studied by varying the $[\text{H}^+]$

Fig. 1 **a** Effect of $[\text{Alamine 336}]$ on Fe(III) & Co(II) extraction from WLL in 10% isodecanol and kerosene. **b** plot of $\log D$ vs $\log[\text{Alamine 336}]$



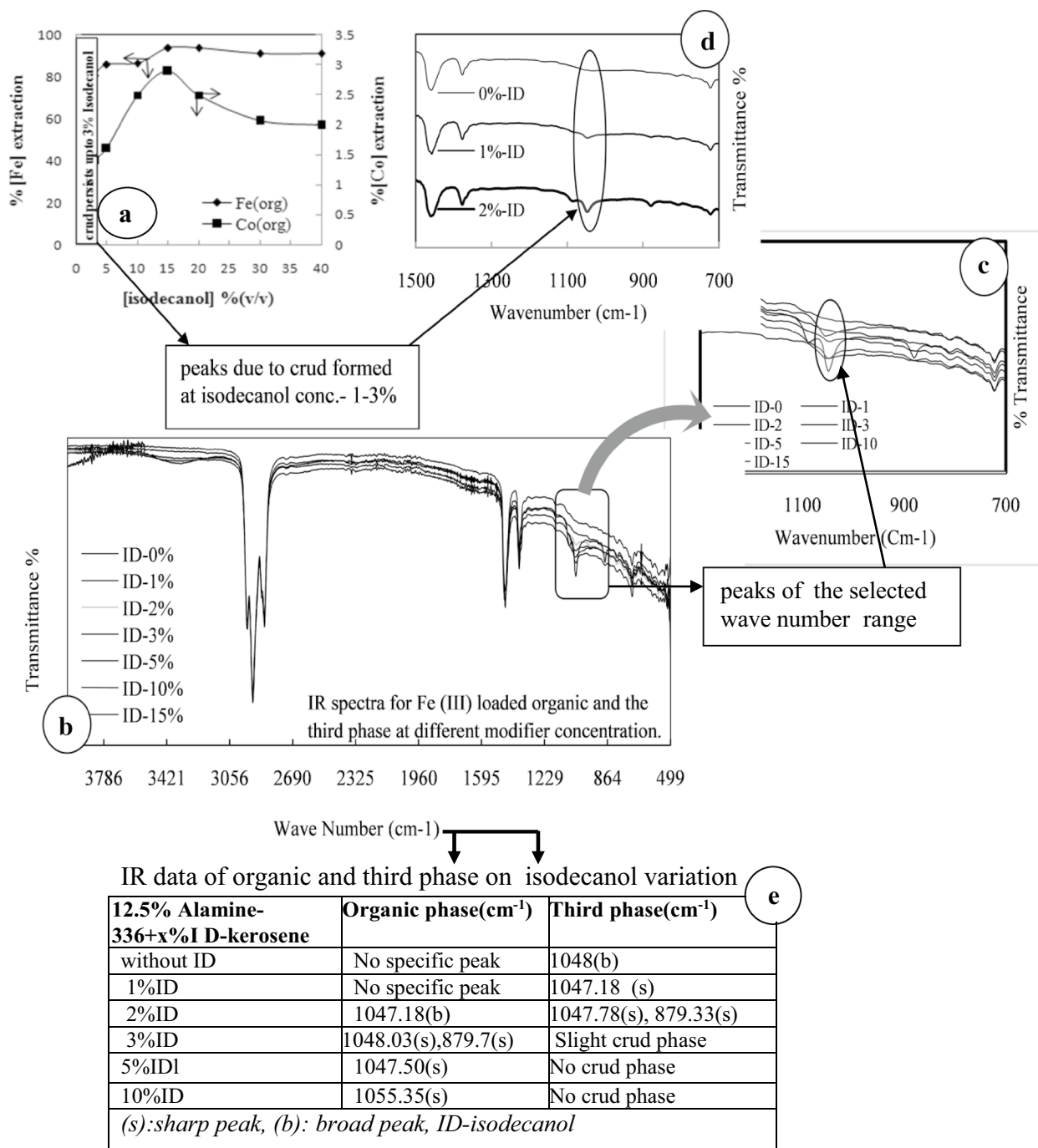


Fig. 2 Effect of concentration of isodecanol on the homogeneity of the organic phase

concentration from 0.5 to 4 M at a constant $[Cl^-]$ concentration of 7.92 M (by adding NaCl). Figure 3 shows that Fe(III) extraction is independent of $[H^+]$ concentration with a co-extraction of 2% Co due to the formation of anionic $CoCl_4^{2-}$ with increasing acidity which could be scrubbed easily. Effect of Cl^- concentration was studied in the range of 1.42–4.92 M by adding NaCl (as a Cl^- source) at 0.5 M HCl at an O/A-1 for 5 min. Figure 3 illustrates an increase in Fe extraction from

27.1 to 97.3% with the increasing $[Cl^-]$ concentration in the aqueous feed with a negligible co-extraction of cobalt. Plot of $\log D_{Fe(III)}$ vs $\log [Cl^-]$ (Fig. 4) demonstrated two slopes at 1.67 in the $[Cl^-]$ concentration range from 1.4 to 2.9 M and 3.59 in the range from 2.9 to 5 M, indicating the association of 2 and 4 mol of the Cl^- with one mole of Fe(III), respectively. These results were substantiated by the report of Good and Srivastava [29].

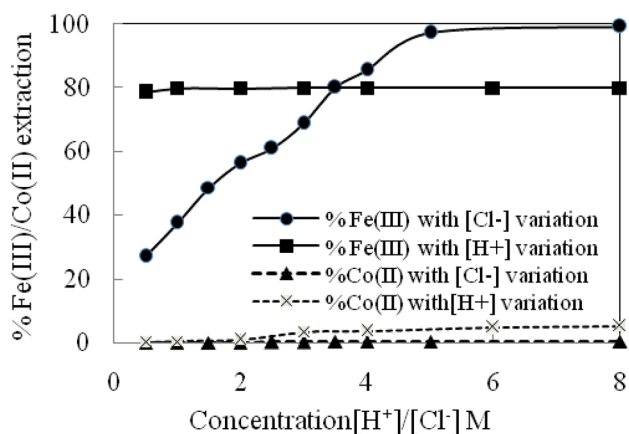


Fig. 3 Effect of $[H^+]$ – $[Cl^-]$ on Fe and Co extraction

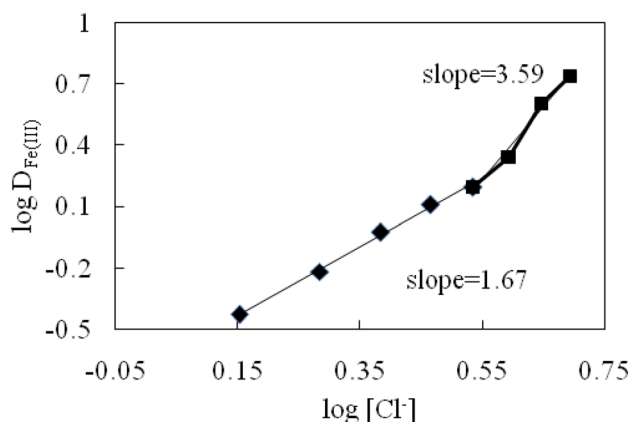


Fig. 4 Plot of $\log D$ vs $\log [Cl^-]$

Effect of Fe(III)/Co(II) Concentration on the Extraction of Fe(III)/Co(II) by Alamine-336

Equal volumes of a synthetic aqueous feed containing a fixed concentration of Co-15 g/L in 4 M HCl with $[Fe(III)]$ varying from 2.5 to 15 g/L and organic phases were contacted for 5-min.

The plot of percent Fe/Co extraction vs $[Fe]$ g/L added(externally) shows a decrease in percent extraction of Fe(III) (Fig. 5a) with the increase in Fe(III) concentration in the aqueous feed with an insignificant co-extraction of Co. In Fig. 5b with an increase in Co concentration from 0 to 15 g/L in 4MHCl, Fe extraction remained constant with a decreasing co-extraction of cobalt.

These results indicate the selective extraction of Fe(III) in presence of a high concentration of Co as present in the WLL. The separation factor for Fe/Co > 1 further indicates the preferential extraction of Fe(III) over Co by this solvent. The separation factor (β_{Fe-Co}) for both the metals is depicted by the following equation:

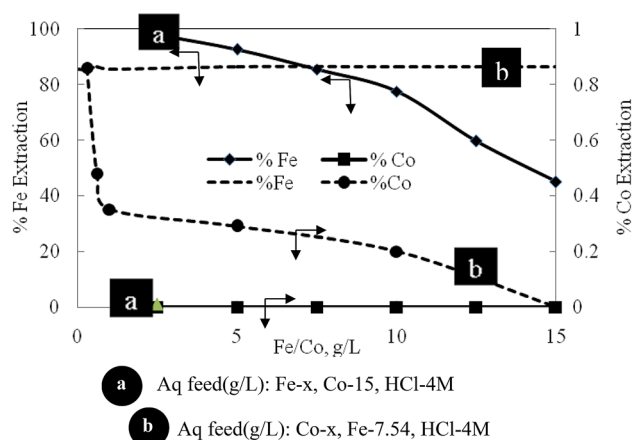


Fig. 5 Effect of Fe and Co concentration on Fe(III) extraction

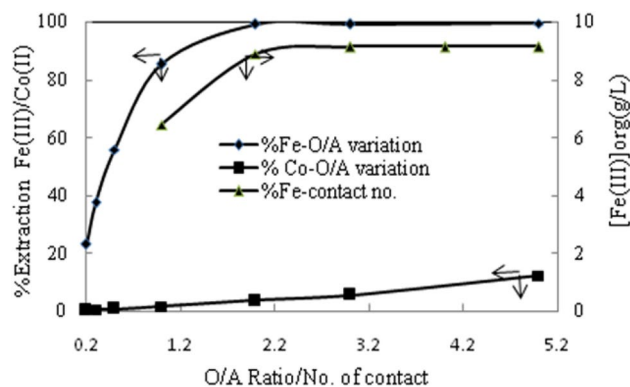


Fig. 6 Loading capacity and O/A variation of 12.5% Alamine 336–10% isodecanol-kerosene from WLL, time-5 min

$$\beta_{Fe-Co} = D_{Fe}/D_{Co}, \quad (4)$$

where β is the separation factor and D_{Fe} , D_{Co} are the distribution coefficient for Fe and Co(Eq-1).

Under the optimized conditions, β_{Fe-Co} for this system was evaluated as 2.14×10^6 (99.9% Fe(III) and 0.4% Co) indicating a high preference of Alamine-336 + isodecanol + kerosene for Fe(III).

Effect of O/A Ratio and Establishment of Extraction Isotherm

Variation of O/A from 1/5 to 5/1 keeping contact time at 5 min (Fig. 6) shows that Fe extraction increases from 23 to 100% with the increase in phase ratio from 1/5 to 2/1.

Since the percent Fe(III) extraction at O/A-1 was 86%, it was selected for all the experimental study. The maximum iron extraction capacity of this solvent was determined by a repeated contact of the same organic solvent

with the fresh WLL up to five contacts. Figure 6 shows that maximum Fe(III) extraction takes place in three contacts.

The optimum O/A and the number of stages required to achieve a quantitative extraction of the metal ions from the aqueous feed was obtained from McCabe–Thiele plot. The extraction isotherm was obtained by plotting $[Fe(III)_{org}]$ vs $[Fe(III)_{aq}]$ at phase ratios ranging from 5:1 to 1:5 for 5 min at a constant total phase volume. A vertical working line was drawn at the intersection on the x -axis corresponding to the initial Fe(III) concentration in the aqueous phase at 7.54 g/L and the operating line for the quantitative extraction of Fe(III) was drawn corresponding to O/A-1:1.1. The plot indicates the requirement of three theoretical stages for the selective extraction of Fe(III) at O/A-1:1.1(Fig. 7).

A three-stage counter-current(CC) extraction was simulated at O/A = 1:1.1, to generate the loaded organic (LO) with 7.53 g/L Fe and 65 mg/L Co (Fig. 8) after 3rd stage and the raffinate was left with Co-14.93 g/L and Fe-8 mg/L.

Scrubbing of Co from the Iron Loaded Organic Phase

After CCS the loaded organic contained 7.53 g/LFe and 65 mg/LCo. The co-extracted cobalt was scrubbed to break and remove the cobalt-solvent complexes to purify the Fe loaded organic. Scrubbing was carried out by two approaches,

- (1) by distilled water at varying acidity from 0 to 5 M
- (2) by varying concentration of $FeCl_3$ from 0 to 10 g/L in the acid range of 0–4 M which would replace the co-extracted Co by Fe.

Scrubbing study was carried out at O/A-10:1 for a contact time of 5 min with both the options. Scrubbing of Co decreased with the increase in scrubber acidity (Fig. 9).

However, a reverse order was observed with $FeCl_3$ solution in the concentration range of 0–10 g/L at varying acidity ranging from 0 to 4 M (Table 2). Thus, 10 g/L Fe(III) in 4 M HCl was reported to be the best scrubber for cobalt removal. WLL could be used as scrubber but we assumed that there

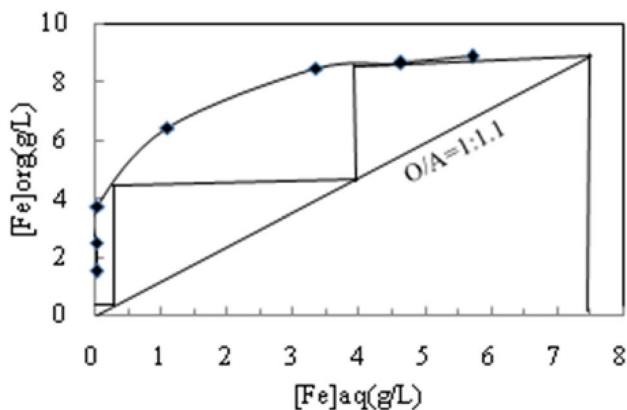


Fig. 7 McCabe–Thiele plot of Fe(III) extraction from WLL. Extractant: 12.5% Alamine 336 10% isodecanol-kerosene, time-5 min

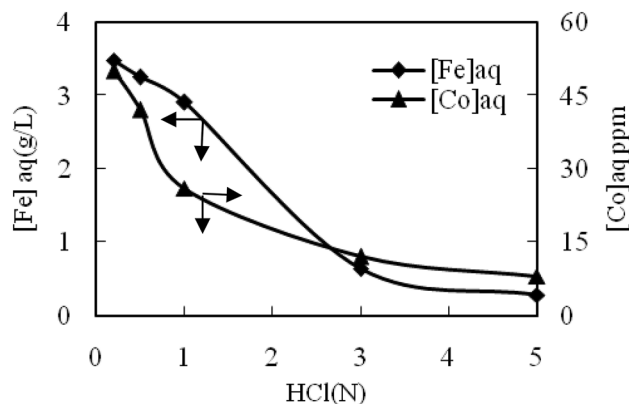


Fig. 9 Scrubbing of Co by varying [HCl] LO(g/L):Fe-7.53, Co-0.065, O/A-5/1, time-5 min

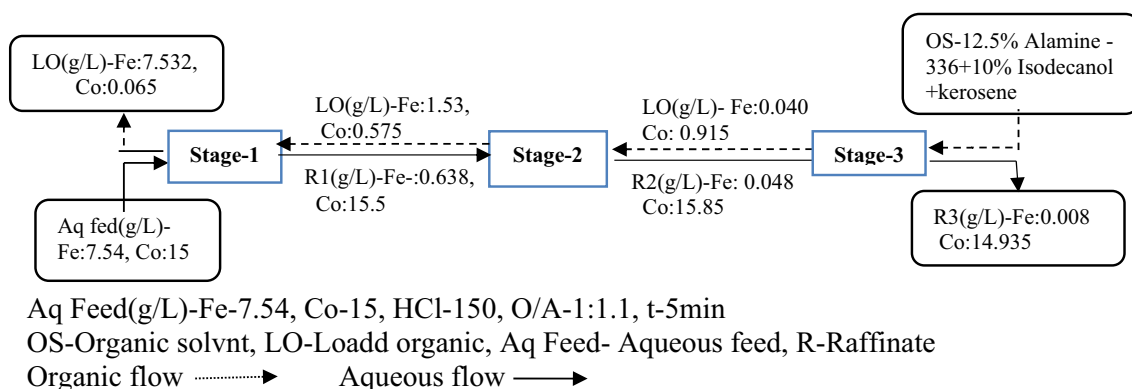
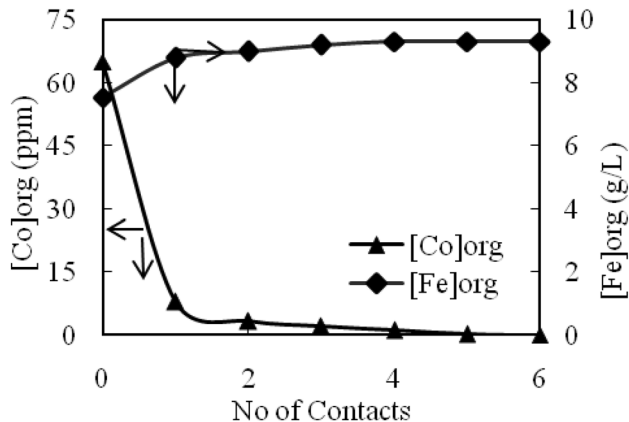


Fig. 8 Counter current extraction of iron using 12.5% Alamine 336+10% isodecanol in kerosene

Table 2 Metal concentration in raffinate after scrubbing with varying concentration of iron in xN HCl

	Fe(g/L)	Concentration of HCl (N)					
		0	0.2	0.5	1	2	4
0	Fe(g/L)	3.9	3.23	3.01	2.7	0.39	0.02
	Co(mg/L)	45	50	42	26	14	10
5	Fe(g/L)	4.95	4.6	4.5	3.5	2.64	2.48
	Co(mg/L)	58.5	55.0	53	51.7	45.5	42.0
10	Fe(g/L)	5.24	4.9	4.76	3.72	3.24	1.34
	Co(mg/L)	62	60.5	58	57.2	56.7	55

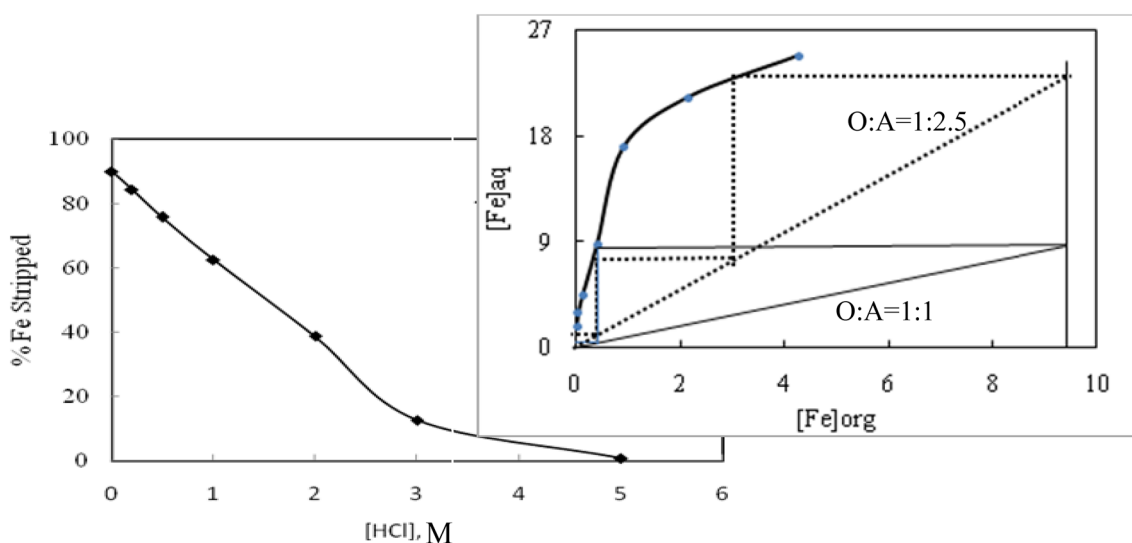
**Fig. 10** Scrubbing of Co by 10 g/L Fe(II) in 4 M HCl in varying contacts, time-5 min

would be a tendency for the extraction of cobalt due to its presence in a large amount. Finally, the scrubbing experiment in the counter-current (CC) mode with 10 g/L Fe(III) in 4 M HCl generating a loaded organic containing 9.23 g/L

Fe(III) and 2 mg/L Co corresponding to 97% scrubbing efficiency in three stages (Fig. 10). During scrubbing, Co from the loaded organic was replaced by about 1.70 g/L of Fe(III). The scrubbed aqueous could be recycled with the WLL.

Since the scrubbing was performed at O/A-10:1, the volume of WLL will increase only by 10% and the Fe(III) concentration in the final feed solution would become 7.61 g/L instead of 7.54 g/L. This negligible change in Fe(III) concentration (0.06 g/L) will not make much difference in the operating conditions and the output stream concentration.

Finally, the scrubbed Alamine-336 was subjected to Fe(III) stripping and the parameters were optimized to recover a pure iron solution for further use. Stripping of Fe(III) at varying HCl [0–5 M] concentration showed a decrease in Fe(III) stripping with increasing acid concentration (Fig. 11), which may be attributed to the formation of extractable Fe(III)-chloro-complex(es). However acidic water at pH-3 could strip the loaded Fe completely and was used in further studies. The stripping isotherm was obtained by plotting $[\text{Fe(III)}]_{\text{stripped aq}}$ vs $[\text{Fe(III)}]_{\text{loaded organic}}$ at varying O/A ranging from 5:1 to 1:5 at a constant total phase volume to find out the number of

**Fig. 11** Effect of HCl concentration on the stripping of loaded Fe(III) and McCabe–Thiele plot for Fe(III) stripping from loaded extractant(g/L) Fe-9.23, Co-0.002, Water-pH 3, t-5 min

stages and O/A ratio to strip out maximum amount of Fe from the loaded organic phase. The McCabe–Thiele plot (Fig. 11) predicts the requirement of two and three counter current stages at O:A ratio of 1 and 1:2.5, respectively, for about 99% of iron stripping which is about 9.14 g/L Fe(III).

An interaction between Alamine-336 and Fe(III) in leach liquor was studied by FTIR spectra of the organic solvent before, after Fe loading and after Fe(III) stripping, recorded in the range of 4000–400 cm^{-1} . IR spectral data and the spectra are given in Table 3. The –C–H symmetric and asymmetric deformation vibrations and stretching vibrations for pure and Fe-loaded Alamine-336 are similar. The characteristic peak for quaternary amine due to $(\text{CH}_3)\text{N}^+$ at 1458.18 cm^{-1} was observed in both the spectra. However, the peak at 1055.35 cm^{-1} due to –C–N stretching vibration for Alamine-336 is shifted to 1047.18 cm^{-1} in the Fe loaded Alamine-336 indicating the weakening of the –C–N bond. The identical peak values for pure Alamine-336 and after stripping (not given in Table 3) confirm the complete stripping of iron. Absence of chemical interaction between the solvent and Fe(III), makes the stripping of Fe(III) very easy with acidic water at pH 3. The stripped Alamine-336 was recycled with the same extraction percentage indicating that the extraction properties of Alamine-336 remains unaffected after several extraction-stripping cycles.

A pictorial representation of the process steps for the extraction and separation of Co and Fe from the acidic filtrate generated on acid leaching of the WC-scrap for tungsten recovery, by solvent extraction route using Alamine-336 is depicted in Fig. 12.

Conclusions

A process has been developed for the selective separation and recovery of cobalt and iron from a highly acidic leach liquor containing(g/L): Fe-7.54, Co-15 in HCl-4 M, generated during the processing of tungsten-carbide scraps.

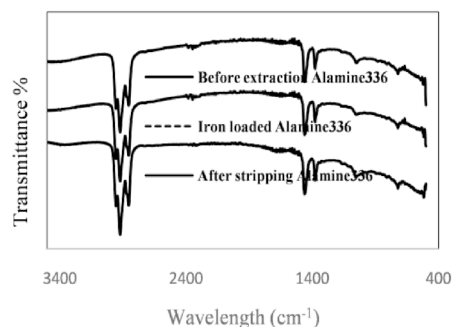
Various parameters affecting the extraction process such as equilibrium time, concentration of Alamine-336, isodecanol, acid, chloride, metal ion and O/A ratio were optimized. Under the optimized conditions the solvent containing 12.5% Alamine-336 + 10% isodecanol + kerosene extracted about 99.9% iron selectively at an O/A-1:1.1 contacted for 5 min, in 3 stages with a co-extraction of 0.2% Co. The separation factor ($\beta_{\text{Fe-Co}}$) was 2.14×10^6 with 99.9% Fe and 0.2% Co extraction. Two slopes from the plot of $\log D_{\text{Fe(III)}}$ vs. $\log[\text{Alamine-336}]$, indicates the formation of two different types of Fe-Alamine-336 complex in different concentration ranges of the solvent. Fe extraction is $[\text{Cl}^-]$ dependent and independent of $[\text{H}^+]$ concentration. The stoichiometry of the extracted species can be given as $[(\text{R}_3\text{NH})_3:\text{FeCl}_4]$ was confirmed by IR spectra. The loading capacity of Alamine-336 under optimized conditions was 7.53 g/L Fe + 65 mg/L Co, which increases to 9.23 g/L Fe + 2 mg/L Co after scrubbing.

Fe from the loaded organic was stripped with water at pH 3. McCabe–Thiele plot shows the requirement of 3-stages for the extraction of 99.9% Fe and complete stripping is possible in two and three stages at O/A ratio of 1, 1:2.5, respectively.

Finally, two aqueous streams containing(g/L): Fe-9.14 + Co-0.00192 in the strip solution and Co-14.93 + Fe-0.008 in raffinate could be used to produce commercially saleable and useable products via-a-vis maintaining environmental safety. The acid left after Co recovery and regenerated solvent could be recycled to the leaching stage and the extraction unit, respectively. Based on the number of experiments performed to optimize the favourable condition it can be concluded that this process seems to be feasible for the selective extraction and separation of Fe and Co from a highly acidic leach liquor. However, a large-scale upgradation of this work needs to be performed to understand its techno-economic viability. This process may be integrated with the tungsten extraction process for recovery of Co, Fe and acid values.

Table 3 IR spectrum and spectral data of organic solvent and iron loaded solvent

Bonds detected	Alamine 336	Fe-Alamine 336
–C–H (sv)	2954.25	2954.08
–C–H (sv)	2853.89	2854.10
–C–H (Asv)	2922.16	2922.15
–C–H (Adv)[–CH ₂ bending]	1458.18	1460.59
–C–H(sdv)[–CH ₃ bending]	1376.93	1377
–C–N (sv)	1055.35	1047.18
–N–H (sdv)	721.58	721.63
[out of plane bending]		
Sv stretching vibration; sdv symmetric deformation vibration; Adv asymmetric deformation vibration		



IR spectrum of Alamine 336 before extraction, Fe loaded Alamine 336 and Alamine 336 after stripping loaded Fe

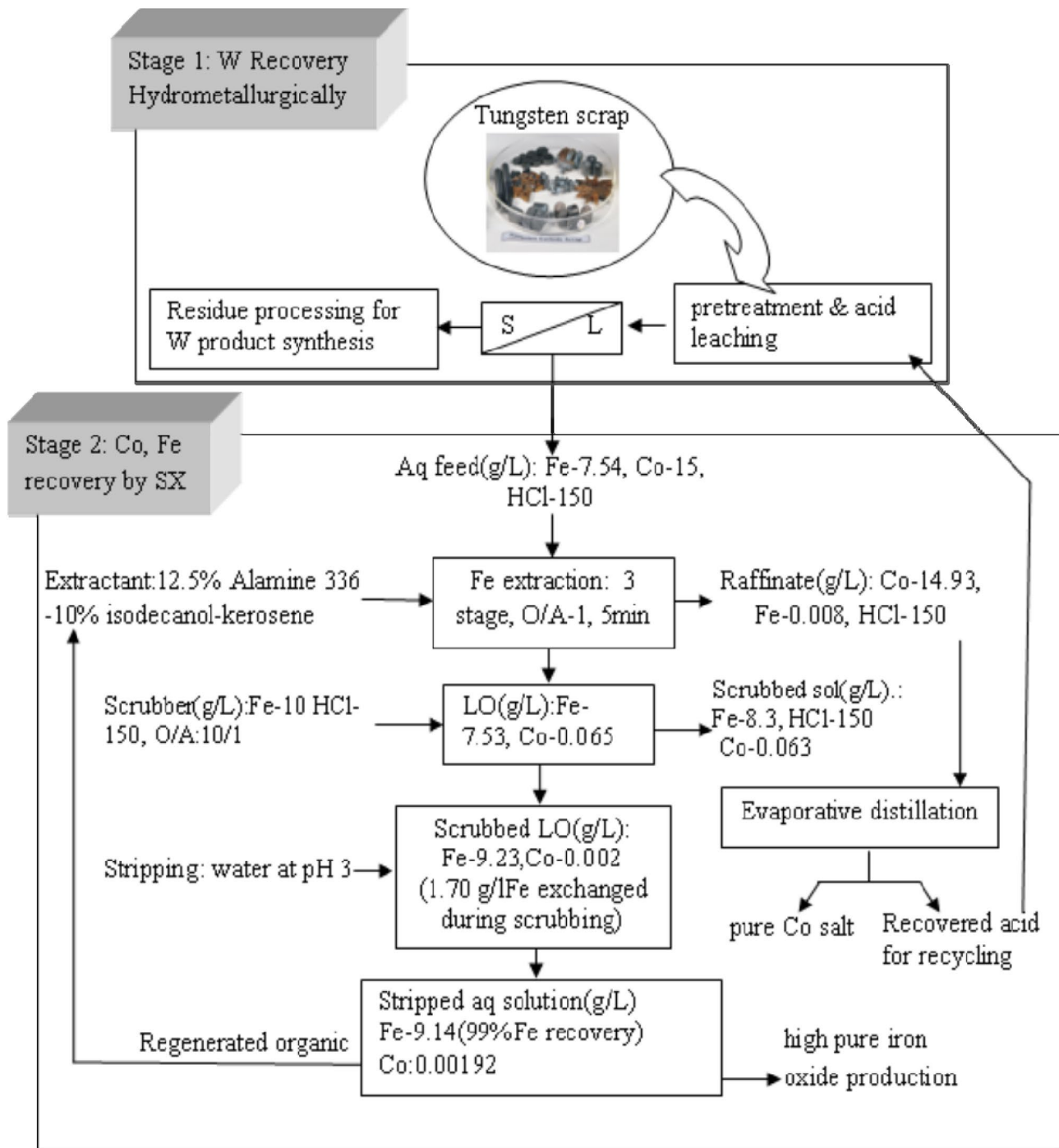


Fig. 12 A pictorial representation of the process steps for the extraction and separation of Co and Fe from WLL by Alamine 336

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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