Separation of Manganese and Iron from Reductive Leaching Liquor of Electric Arc Furnace Dust of Ferromanganese Production Units by Solvent Extraction

Behzad Ghafarizadeh [1] and Fereshteh Rashchi [*1]

[1] School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran

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Abstract

Electric arc furnace dust (EAFD) of ferromanganese production units, in the form of slurry, contains tar, alkalies, manganese, zinc, iron, silica, calcium, aluminum and other elements. A hydrometallurgical route based on solvent extraction technique was investigated for selective separation of manganese from the dust. Leaching of the EAFD resulted in an aqueous feed containing 4 g/L of manganese and 0.87 g/L iron. At the next stage, extraction of manganese and iron from the leach liquor was performed using D2EHPA, Cyanex 272, Cyanex 302 and their mixtures in various proportions. The synergistic effect of the extractants on the separation of iron and manganese with a mixture of D2EHPA and Cyanex 272 or Cyanex 302 was studied. Increasing the Cyanex 272/ 302 to D2EHPA ratio in the organic phase increased the distance between the extraction isotherms of manganese and Iron. The highest separation factor of iron over manganese was obtained with 15:5% v/v of Cyanex 302: D2EHPA mixture. Effects of various aromatic and aliphatic diluents, such as hexane, kerosene, and carbon tetrachloride on the extraction were also investigated.

Keywords: Solvent extraction, EAFD, D2EHPA, Cyanex 272, Cyanex 302, Synergistic effect

Introduction

Electric arc furnace dust (EAFD) of ferromanganese production units is formed from volatiles and fines collected during wet scrubbing of the off-gas from manganese alloy smelting furnaces. This dust, contained about 24% manganese and 10% iron, could be used as secondary manganese sources. Iron (II) is the major impurity leached with manganese from EAFD during reductive leaching process [1]. Iron, having some similar chemical properties with manganese, constitutes a severe impurity in manganese solution; therefore, an efficient process must be used for the separation of manganese and iron.

In recent decades, solvent extraction has been successfully used for purification and separation surveys in leach liquors containing manganese. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is a relatively cheap and stable organic extractant with low aqueous solubility. It is the most widely used extractant for manganese [2-6]. The extraction reaction of a divalent metal (M^{2+}) with D2EHPA can be represented by the following general equation [2]:

$$M^{2+}+2(HA)_2=MA_4H_2+2H^+ \qquad (1)$$

Where HA stands for D2EHPA in the organic phase and MA_4H_2 is the metal–organic complex in the organic solution. The metal extraction as a function of pH_{50} (the equilibrium pH value at which 50% extraction of each metal has occurred) lies in the order (pH_{50} in brackets) [2]:

Zn(1.7)~Ca(1.72)>Mn(2.71)>Cu(2.80)>Co(3.7)>Ni(3.82)>Mg(4.3)

D2EHPA has been used for the separation of manganese from cobalt and nickel and can also be applied for the separation of zinc, beryllium, copper, vanadium, indium, gallium and rare earth elements [2]. Removal of iron with D2EHPA from different acid solutions has been studied [7, 8]. Iron (III) was easily extracted by D2EHPA however striping of this metal from loaded extractant was found to be very difficult [8]. Extraction of iron (II) from sulfate solutions was investigated and it is reported that this metal ion is readily stripped from D2EHPA [3, 8].

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* Corresponding author: Tel: +98- 21-88012999 Fax: +98- 21-88006076 Email: rashchi@ut.ac.ir

Extraction of manganese with bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) has been extensively studied [2,4-6, 10-12]. The extraction of metals from a sulfate medium with Cyanex 272 in toluene was established in the order (pH_{50} in brackets) [13]:

Zn(2.51)>Cu(4.13)>Mn(4.06)>Co(4.65)>Mg(5.59)>Ca(6.15)>Ni(6.58)

Previous studies have shown that Cyanex 272 is a good extractant in terms of separation of cobalt from nickel, zinc from manganese, and manganese from nickel [2, 10 and 11]. Bis (2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) was first used for the extraction of zinc from sulphate solutions containing calcium [13]. It also has been successfully used for extraction of manganese [14] and iron [15, 16]. Using this extractant, the extraction equilibria of manganese can be best described by assuming the formation of the extracted complex $MnR_2(RH)_4$ in the organic phase [14]. The extraction of iron (III) with Cyanex 302 was possible with very low concentrations of the reagent compared with other methods [15].

Recently, researches have shown that using a mixture of extractants affects the manganese separation more than a single extractant [6, 17, and 18]. Adding Cyanex 302 to D2EHPA caused a synergistic effect and shifted the extraction curve of zinc to lower pHs and manganese to higher pHs, thus, separation of manganese from zinc improved [6, 17]. The extraction of iron (III), iron (II) and zinc (II) with mixtures of TBP (Tri-butyl phosphate)/ D2EHPA and Cyanex 302 from hydrochloric acid solutions was studied. Iron (III) could be selectively extracted with the mixtures of TBP with D2EHPA or Cyanex 302 [16].

Reductive leaching of manganese from EAFD, using hydrogen peroxide (H_2O_2) and oxalic acid as reducing agent was separately investigated [1]. Fig. 1 shows the flowchart of the hydrometallurgical route proposed for the recycling of manganese from EAFD. As it can be seen from Fig. 1, this route comprises the following main steps: water leaching, reductive leaching and solvent extraction. In this research solvent extraction and separation of iron and manganese were studied. Effect of pH, type of organic extractants, diluents and modifier were also determined in order to develop a new process for selective separation of manganese and iron from leach liquor.

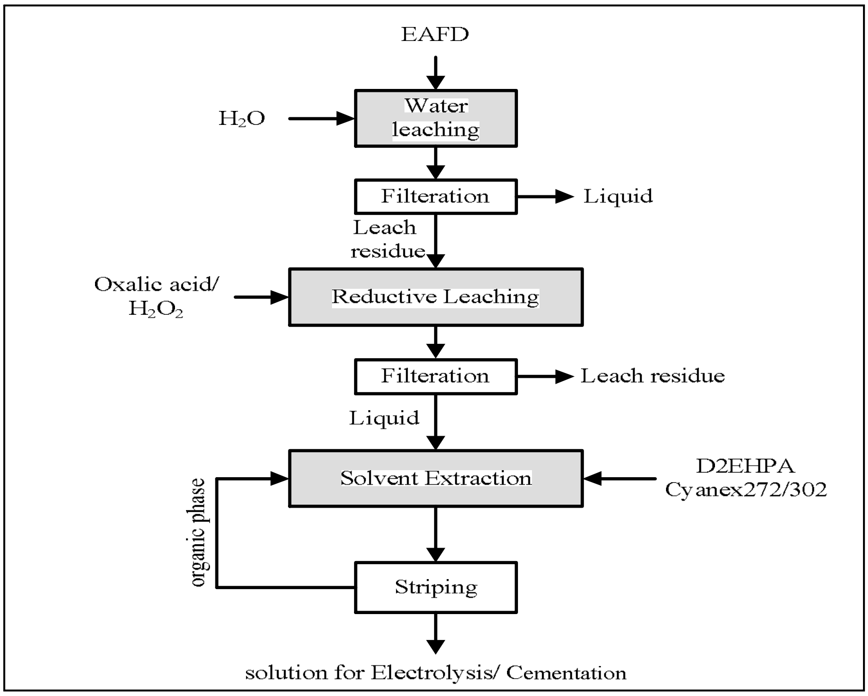

Figure 1: Hydrometallurgical route proposed for the recycling of manganese from EAFD

1. Experimental

1.1. Aqueous solution

Sulfuric acid (98% pure), iron (II) sulfate (97% pure) and manganese sulfate (98% pure) were obtained from Merck, Germany. A synthetic aqueous solution of 4 g/L manganese and 0.87 g/L iron was prepared by dissolving sufficient amount of iron (II) sulfate ($FeSO_4$) and manganese sulfate ($MnSO_4$) salts in distilled water. This ratio of the metals was obtained from the optimum leaching condition, in the presence of 0.31 mol/L oxalic acid as reducing agent, for the EAFD leaching determined in a previous work [1]. A small amount of sulfuric acid was added to the solutions to prevent hydrolysis of the metal ions and to adjust pH to ca. 0.5 (to simulate the pH of the leach solution in the previous research [1]).

1.2. Organic solution

The organic solvents used in this research were D2EHPA (97% pure) from Bayer, Germany, Cyanex 272 and Cyanex 302 (98% pure) from Fluka, Canada. These organic extractants were used as received without any further purification. Kerosene (mostly aliphatic in nature, from Tehran Oil Refinery), Hexane and Carbon tetrachloride (from Merck, Germany) were used as diluents. TBP (98% pure) added to the extractant solution in kerosene to act as a phase modifier was provided by Merck. The level of TBP was kept at 5%(v/v) in the extractant.

1.3. Solvent extraction experiments

A plexi glass rectangular box (10×10×15(H) cm^3) immersed in a thermostatically controlled water bath was used for mixing the organic and aqueous solutions using overhead stirrers to obtain a good mixing of the two phases. Each experiment was carried out by contacting 200 mL of aqueous solution and 200 mL of organic solution containing 20%(v/v) of the organic extractant (D2EHPA, Cyanex272/302 or their mixture) in 80%(v/v) diluent for 10 minutes after pH was stable. Sulfuric acid and ammonia solution (25%) from Merck, Germany, were used to adjust the solution pH as required. A PY-11 pH meter from Sartorius made in Germany was used to monitor pH during the experiments. Experiments were carried out at room temperature (23°C). After 10 minutes of mixing, 20 mL of the mixture of organic and aqueous phases was transferred to a separatory funnel.

McCabe–Thiele plots for extraction were constructed while keeping the A: O ratios within 2:1 and 1:5 and total volume of the phases constant.

1.4. Chemical analysis

After separating the aqueous and organic phases, about 10-mL of the aqueous solution was taken for chemical analysis. Manganese and iron concentrations in the aqueous solution were determined by standard titration methods using EDTA (ethylenediaminetetraacetic acid) [19]. Eriochrom black T is used as indicator for manganese measurement. For determining the oxidation number of leached iron, two different titration methods are used. Potassium permanganate ($KMnO_4$) and salicylic acid were used as indicators for iron (II) and iron (III) measurements, respectively. Eriochrom black T, EDTA, salicylic acid, and potassium permanganate were obtained from Merck, Germany. The concentration of manganese and iron ions in the organic phase was calculated from the difference between concentrations of metals in the aqueous phase before and after extraction by mass balance.

2. Results and discussion

2.1. Effect of equilibrium pH and kind of organic extractant

To investigate the effect of equilibrium pH, extraction of manganese and iron was studied in the pH range of 0.5 -6.0 with an A:O ratio of 1:1 at room temperature (23°C), using 20% of either D2EHPA, Cyanex 272 or Cyanex 302 in kerosene. The distribution coefficient (D), the percentage extraction (%E) and separation factor of manganese and iron ($\beta_{Fe/Mn}$) at different pH values were determined. The distribution coefficient is the ratio of concentration of metal ions present in the organic phase to that in the aqueous phase at equilibrium state. The percentage extraction is calculated from the following equation [20]:

$$\%E = \frac{D \times 100}{D + \left(\frac{V_{aq}}{V_{org}}\right)} \qquad (2)$$

Where V_{aq} and V_{org} are the volumes of aqueous and organic solution, respectively.

The separation factor (β) is a measure of selectivity in the extraction of iron and manganese. This factor is defined as [20]:

$$\beta_{Fe/Mn} = \frac{D_{Fe}}{D_{Mn}} \qquad (3)$$

Separation factor and ΔpH_{50} (difference between iron and manganese pH_{50}) for all the cases studied in the present work are listed in Table 1.

Table 1: ΔpH_{50} and $\beta_{Fe/Mn}$ using different D2EHPA and Cyanex 272 or 302 mixtures

Extractant	D2EHPA: Cyanex 302/272 (%v:v)	ΔpH_{50}		pH								
				0.5	1	1.5	2	2.5	3	3.5	4	4.5
D2EHPA	20:0	0.4	$\beta_{Fe/Mn}$	1.83	1.57	1.73	1.83	2.64				
Cyanex 272	0:20	1.3	$\beta_{Fe/Mn}$		2.07	2.13	2.75	3.82	4.94	6.52	8.05	
Cyanex 302	0:20	2.1	$\beta_{Fe/Mn}$	6.50	4.66	4.57	4.70	5.50	6.64	8.47	12.65	38.52
Mixture of D2EHPA and Cyanex 272	15:5	0.8	$\beta_{Fe/Mn}$	2.75	2.52	2.56	3.07	4.65				
	10:10	0.4	$\beta_{Fe/Mn}$		36.00	7.00	3.65	7.13				
	5:15	1.4	$\beta_{Fe/Mn}$	10.60	9.00	8.75	7.63	8.50	15.50			
Mixture of D2EHPA and Cyanex 302	15:5	0.5	$\beta_{Fe/Mn}$	2.42	3.33	2.80	2.83	2.81	14.80			
	10:10	0.9	$\beta_{Fe/Mn}$	5.20	3.11	3.38	2.73	3.60	9.86			
	5:15	1.3	$\beta_{Fe/Mn}$	2.60	2.50	2.53	2.76	3.45	8.83	30.50	82.92	

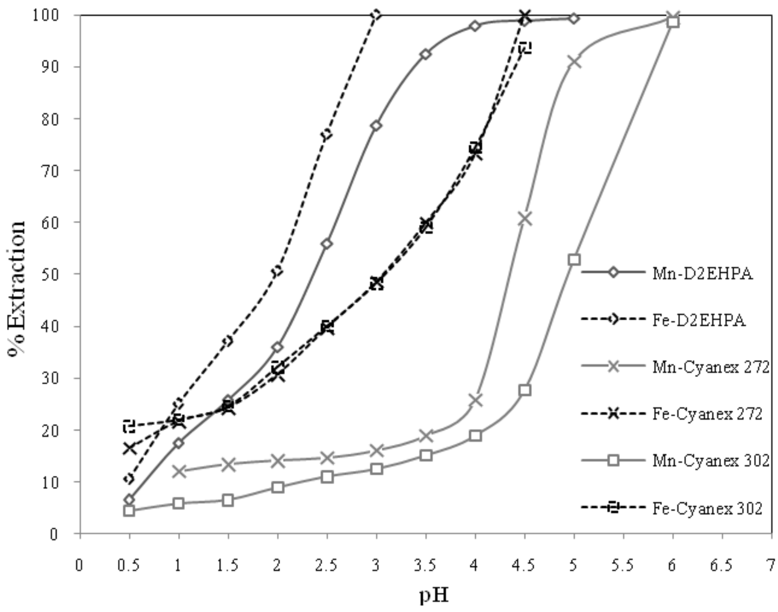

Figure 2: Effect of equilibrium pH on extraction of iron and manganese using 20% of either D2EHPA , Cyanex 271 or Cyanex 302 and 80% kerosene at 23°C and A/O ratio of 1:1

Figure 2 shows pH-extraction isotherms of manganese and iron (II) at 23°C using 20% D2EHPA, Cyanex 272 or Cyanex 302. As it can be seen, the percentage of extraction was increased with increasing equilibrium pH for both metal ions. This result is consistent with other studies published in literature [6, 17].

In the case of extraction with D2EHPA, the pH_{50} values were 2 for iron and 2.4 for manganese. Therefore, iron was extracted at a lower pH compared to manganese. According to Table 1, the highest separation factor of 2.64 was obtained at an equilibrium pH of 2.5. The low amount of ΔpH_{50} (0.4) and separation factor indicates that separation of manganese from iron is not possible at that condition. The value of ΔpH_{50} is an indication of a possible separation method for the metal ions.

In case of extraction with Cyanex 272, the pH_{50} values were 3.1 and 4.4 for iron and manganese, respectively (ΔpH_{50}=1.3). The highest separation factor of 8.05 was obtained at an equilibrium pH of 4.

Using Cyanex 302, the pH_{50} values were 3.1 for iron and 5.2 for manganese (ΔpH_{50}=2.1). The highest separation factor of 38.52 was observed at an equilibrium pH of 4.5. Therefore, based on the results of separation factor and $\Delta pH_{50,}$ Cyanex 302 is suggested as an organic extractant for separation of manganese and iron from solutions at a condition similar to the one studied here.

2.2. Synergistic effect of organic extractant

Figs. 3 and 4 illustrate the extraction isotherms of manganese and iron using different D2EHPA and Cyanex 272 or 302 mixtures with a fixed total extractant concentration of 20%(v/v) (~0.6 M). As can be seen from the Figs. 3 and 4, increasing the Cyanex 272/ 302 to D2EHPA ratio in the organic phase caused a right shifting (to higher pHs) of extraction isotherms of manganese and iron. Right shifting of manganese isotherms were more than that of iron isotherms; thus, addition of Cyanex 272/302 to D2EHPA improved separation of iron over manganese. Table 1 shows ΔpH_{50} and the separation factors of iron and manganese using different ratios of D2EHPA to Cyanex272 or 302. According to Table 1, increasing the Cyanex 272 to D2EHPA ratio to 15:5, the ΔpH_{50} of manganese and iron increased from 0.4 to 1.4 and the separation factor from 2.64 at pH 2.5 to 15.5 at pH 3. The separation factor of 15.50 was the highest value except the 36.00 at an equilibrium pH of 1 in the case of the ratio of D2EHPA: Cyanex 272 equal to 10:10. However, although the separation factor is high, the extraction of manganese and iron at this pH is negligible (0.5 and 26.5%, respectively), thus, this is not a suitable condition for the extraction and separation of these metallic ions.

As it can be seen from Table1, the highest separation factor (82.92) was achieved at an equilibrium pH of 4 and D2EHPA to Cyanex 302 volume ratio of 1:3. Therefore, a mixture of 5% D2EHPA: 15% Cyanex 302 resulted in a better separation of manganese from iron compared to the mixture of D2EHPA: Cyanex 272 at the same volume ratio.

2.3. Effect of TBP as modifier

Modifiers are sometimes added to the solution to prevent crud (third phase) formation and to enhance phase separation; moreover, they could also affect the metal extraction [20]. Effect of TBP as phase modifier and synergist agent in separation of metals has been reported widely [21, 22]. To determine the effect of TBP as the phase modifier, experiments were carried out in the presence of 15% Cyanex 302: 5% D2EHPA in kerosene (the best ratio of the organic extractants as discussed in section 3.2), at an A:O of 1:1, temperature of 23 °C, and 5% (v/v) TBP. Adding TBP caused the extraction isotherms of manganese and iron to shift slightly (0.1 unit of pH) to the left and right, respectively. Separation factors of manganese and iron decreased from 82.92 (without TBP, at an equilibrium pH of 4) to 8.47 (5% TBP, at equilibrium pH 3.5). Therefore, it seems that using TBP as a modifier decreased the separation factor of manganese and iron in the system studied.

2.4. Effect of diluents

The diluents themselves are unable to extract metal ions from the aqueous solution, but they greatly affect the extraction behavior of the organic solvent [23]. Composition of the diluents influences the distribution of both the neutral metal–organic complex and the extractant, through similar interactions ranging from that of cavity formation for very inert diluents like hexane, through dipole-dipole interactions, pi electron interaction, and hydrogen bonding for the more reactive solvents [20]. Kerosene, hexane and carbon tetrachloride were tested for the extraction and separation of manganese and iron with 15% Cyanex 272: 5% D2EHPA at an A: O ratio of 1:1. Fig. 5 illustrates the effect of different diluents on manganese and iron extraction isotherms. As it can be seen, using carbon tetrachloride as diluent shifted the manganese isotherm to the left and iron isotherm to the right. Table 2 shows ΔpH_{50} and the separation factors of iron and manganese using different diluents. From the results, it is obvious that the maximum values of separation factor (167.33) and ΔpH_{50} of manganese and iron (4.4) were achieved in the presence of carbon tetrachloride as diluent. Therefore, the system with 15% Cyanex 302: 5% D2EHPA/carbon tetrachloride is more effective for iron and manganese separation than the formerly studied systems.

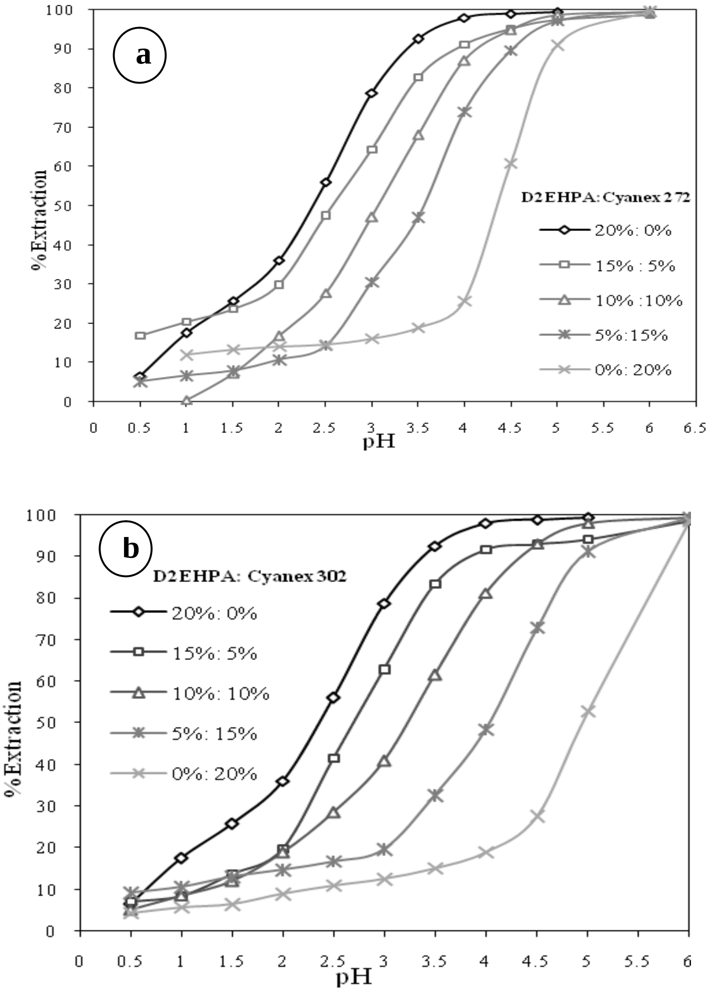

Figure 3: extraction isotherms of manganese at 23°C and 20% v/v of the extractants in kerosene and their mixtures (a) D2EHPA/Cyanex 272 (b) D2EHPA/Cyanex 302

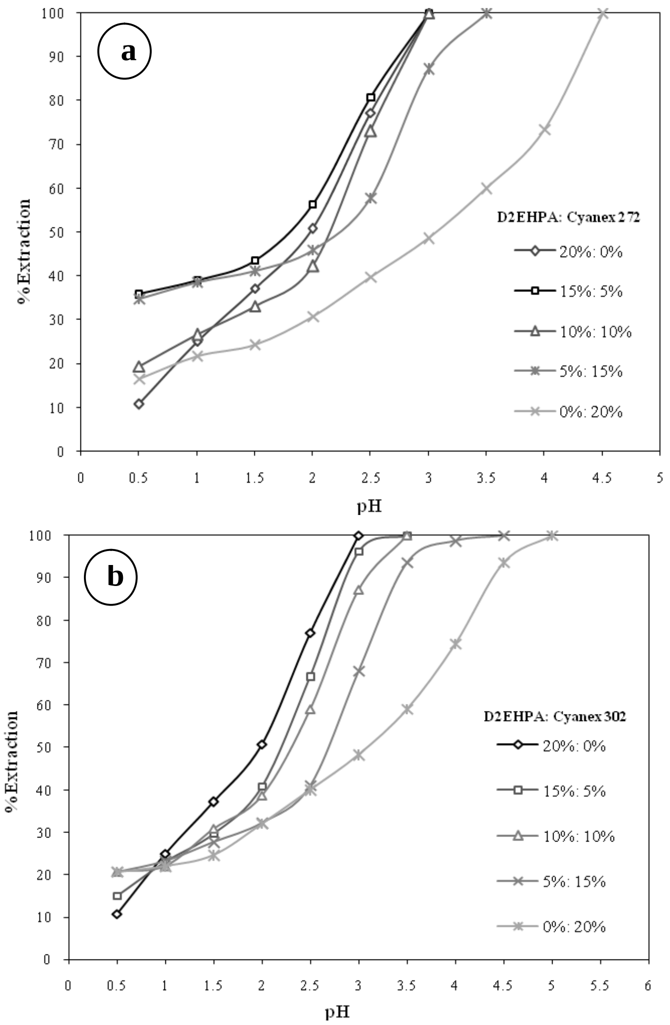

Figure4: extraction isotherms of iron by at 23 °C and20% v/v of extractants in kerosene and their mixtures (a) D2EHPA/Cyanex 272 (b) D2EHPA/Cyanex 302

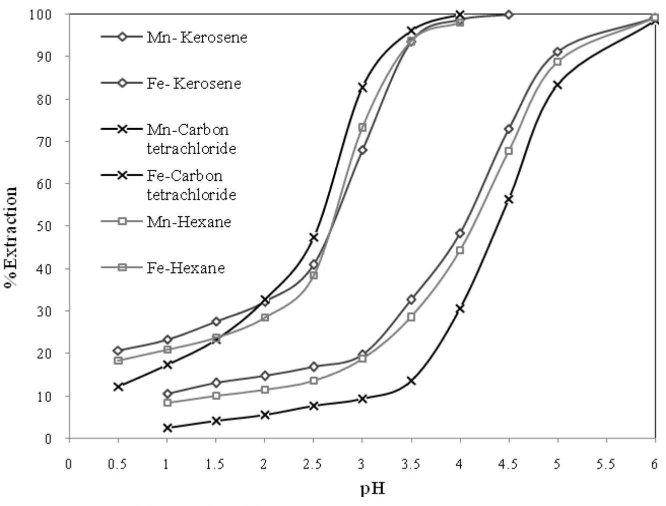

Figure 5: Effect of different diluents on manganese and iron extraction isotherms in 15%Cyanex 302: 5%D2EHPA at A:O ratio 1:1, temperature 23°C

Table 2: ΔpH_{50} and $\beta_{Fe/Mn}$ using different diluents and 15% Cyanex 302: 5% D2EHPA

Diluents	ΔpH_{50}		pH						
			1	1.5	2	2.5	3	3.5	4
Kerosene	4	$\beta_{Fe/Mn}$	2.50	2.53	2.76	3.45	8.83	30.58	82.92
Hexane	4.1	$\beta_{Fe/Mn}$	2.88	2.81	3.07	4.13	11.73	36.22	65.22
Carbon tetrachloride	4.4	$\beta_{Fe/Mn}$	10.50	7.50	9.60	11.25	48.3	167.33	

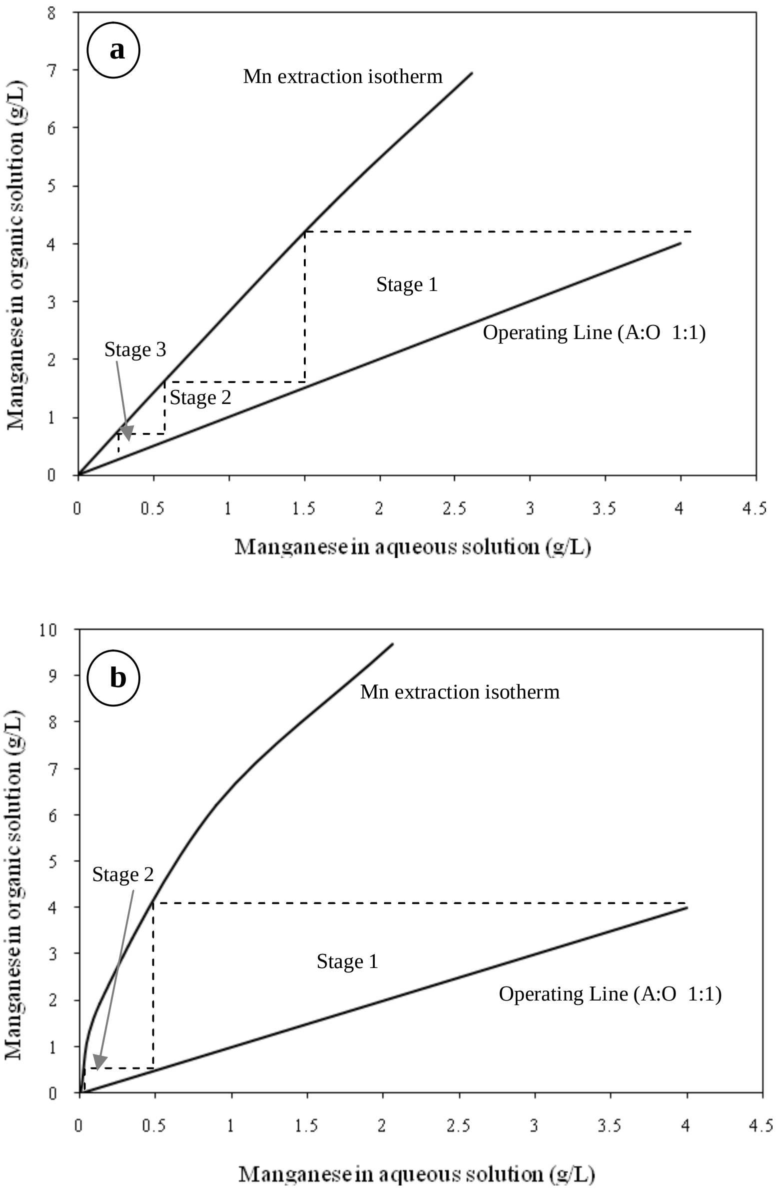

Figure 6: Manganese McCabe–Thiele diagram in 15%Cyanex 302: 5%D2EHPA, temperature 23°C, a) pH 4 b) pH 4.5

2.5. Extraction stages estimated by McCabe–Thiele method

To determine the number of theoretical extraction stages required at A: O ratio of 1:1, McCabe-Thiele diagrams were constructed varying the A: O from 2:1 to 1:5, while keeping the total volume of phases constant. Figs. 6a and 6b show McCabe-Thiele diagrams for extraction of manganese using 15% Cyanex 302: 5% D2EHPA/carbon tetrachloride, at A: O of 1:1, temperature of 23 °C, pHs 4 and 4.5, respectively. Fig. 6a suggests three stages of extraction at an equilibrium pH of 4. Fig. 6b illustrates two stages for extraction of manganese at an equilibrium pH of 4.5.

3. Conclusions

1- Extraction of iron by either D2EHPA or Cyanex 272/302 occured at a lower pH value as compared to manganese. The percentage of extraction enhanced with increasing equilibrium pH for both of the metal ions.

2- Adding Cyanex 272/302 caused a synergistic effect and shifted manganese and iron isotherms to the right. Right shifting of manganese isotherm was more than iron isotherm. Thus, addition of Cyanex 272/302 to D2EHPA improved separation of iron over manganese.

3- Increasing Cyanex 302 concentration, the separation factor of manganese and iron increased to ca. 82.92 at equilibrium pH of 4; therefore, mixture of 5% D2EHPA and 15% Cyanex 302 caused a better separation of manganese from iron as compared to the sole extractant and other extractant mixtures studied in this research.

4- Using TBP as modifier decreased the separation of manganese and iron in the system of 15% Cyanex 302: 5% D2EHPA/kerosene.

5- Using carbon tetrachloride as diluent, maximum values of separation factor (167.33) and ΔpH_{50} (4.4) for manganese and iron separation were achieved. Therefore, 15% Cyanex 302: 5% D2EHPA/carbon tetrachloride was more effective for iron and manganese separation than the other systems studied.

The McCabe–Thiele diagram for the system of 15% Cyanex 302: 5% D2EHPA/carbon tetrachloride showed that at a pH of 4.5 and 23°C, two theoretical extraction stages were required to completely extract manganese from the solution.

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