Extraction of iron (III) from acid solutions got from slag

(Produced after red mud treatment by Krupp-Renn process)
leached away by appropriate sulphuric acid concentrations and extraction of titanium (IV) and other (rare) metals

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An appropriate process of separating present constituents from sulphuric acid solutions got from slag (produced after red mud treatment by Krupp-Renn's process) leached away by the appropriate sulphuric acid concentrations has been developed.

After titanium (IV) and rare metals separation by solvent extraction, partition of iron (III) in presence of iron (II), aluminium (III) and silicon (IV) between the sulphuric acid solutions and solutions of di-(2-ethylhexyl) phosphoric acids was investigated by varying pH (adding sodium hidroxide solution) concentration of aqueous iron and solvent. The variation of pH in the course of the extraction was also investigated. The experiments were made within one mixer-settler stage, i.e. within the mixing part.

The plant counter — current solvent extraction mixer-settler system is designed primarily to separate titanium (IV) and rare metals, and then, possibly, iron (II), iron (III) and aluminium (III) as other constituents, beside silicon (IV) which is out of interest.

1. INTRODUCTION

The problem of separation of titanium (IV) and other rare metals from red mud has been endeavoured to solve by their transference into slag by the red mud treatment according to Krupp-Renn process. After the slag leached away by a sulphuric acid solution of an appropriate concentration, they were separated by a solvent extraction technique in a counter-current solvent extraction mixer-settler system.

As the sulphuric acid solution besides titanium (IV) and rare metals contains also iron (II), iron (III), aluminium (IV) and silicon (IV), the question of their separation imposes.

Experiments within the mixer-settler mixing part with the aim to find out the optimal conditions of iron (III) solvent extraction by di-(2-ethylhexyl) phosphoric acid in kerosene, in presence of iron (II), aluminium (III) and silicon (IV), were made. Reports dealing with this extractant formed the basis for this work [1], [2].

2. EXPERIMENTAL

2.1. Materials

The di-(2-ethylhexyl) phosphoric acid (DEHPA) ("Fluka, A.-G.") was purified by washing several times successively with 10% sodium carbonate solution, 6_M hydrochloric

acid and water. The kerosene used as diluent was also washed successively with concentrated sulphuric acid, dilute sodium hydroxide and water [3].

The sulphuric acid ($0{,}618_M$) for constituting the system was got from slag (produced after red mud treatment by Krupp-Renn process) leached away by the appropriate sulphuric acid concentration and extraction of titanium (IV) and other rare metals. The concentration of every single constituent in the sulphuric acid solution was as follows: iron (II)-1,116 g/l, iron (III)-2,290 g/l, aluminium (III)-4,702 g/l, silicon (IV)-0,130 g/l, whereas the concentration of titanium (IV) and other rare metals was neglectedly low.

Other chemicals for constituting the system were: 99% sodium hydroxide, "A. Merck", analytically pure and water, distillated.

All chemicals and reagents used for analysing the system were analytically pure.

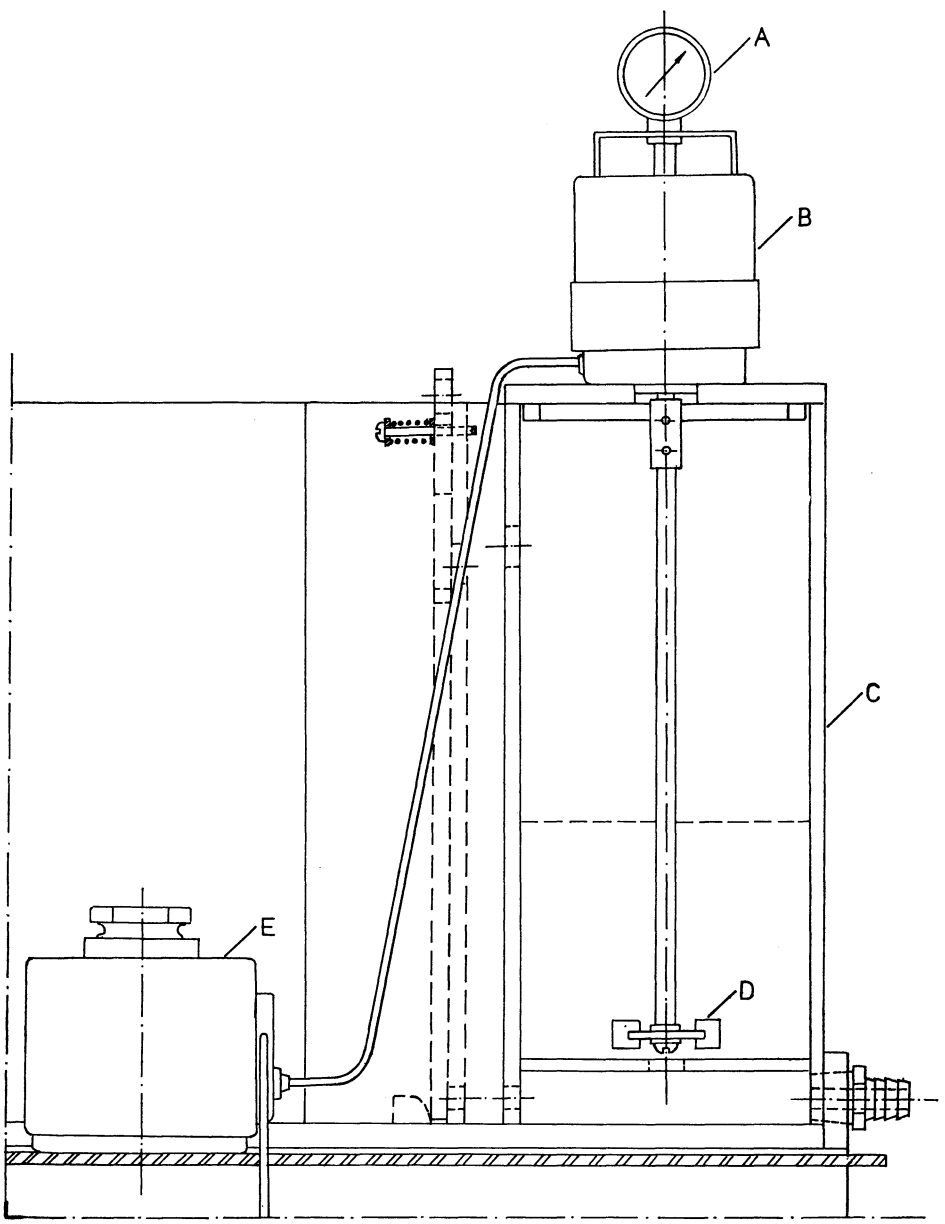

Fig. 1. — Experimental apparatus
A: Tachometer. — B: Motor. — C: Mixer — D: Impeller. — E: Rheostat

2.2. Equipment

The general arrangement of the equipment is shown diagrammatically in Figure 1. The mixing vessel was a part of mixer-settler unit constructed of plexiglass. It was 153 × 153 × 265 mm deep to the overflow.

The turbine impeller was a shrouded, flat blade impeller of conventional design, and had four blades, each 14,9 mm long and 12,7 mm deep, with an outer diameter of 59,2 mm. The impeller diameter was fixed at one-half of the mixing vessel side dimension, in accordance with the recommendation of Rushton [4]. The impeller was carefully centred above the flow inlet, which was during the experiments appropriately sealed, and spaced with a clearance of 7,5 mm above it. The impeller was also fabricated of plexiglass with the impeller shaft fabricated of a special kind of stainless steel. The impeller speed was held always the same by a rheostat and controlled by a tachometer.

2.3. Procedure

The solvent extraction experiments were carried out in the mixing vessel, fed with the phase mixture to the height equal to its diameter. The system was large so the phases were added from mensures with the volume of 2000 ml, calibrated to 20 ml. Each phase was prepared separately, adding single components directly. To accomplish an appropriately fine dispersion of one phase in another, the phases were mixed by a turbine impeller, with the impeller speed held always the same. The experiments were carried out at room temperature of 20 ± 2 °C. To determine the aqueous phase constituents analytically, samples were taken directly. All determinations were made using at least two parallel samples and if they did not coincide the determination was repeated.

To determine the aqueous phase pH values, samples were also taken directly and the pH values were determined pH-metrically by a TTTlc titrate type (Radiometer A/S, Copenhagen NV, Denmark). Electrodes that were used are: a saturated calomel electrode — K400 type, a glass electrode — G200 B type (Radiometer A/S, Copenhagen NV, Denmark) and, for the electrode gauging, pupher titrisol, "A. Merck", of ± 0,02 pH at 20 °C punctuality, examined electrometrically.

3. RESULTS AND DISCUSSION

3.1. Dependance of iron (III) extraction on pH value

Tests at various pH values were carried out with the diluted sulphuric acid consisting of iron (III) — 1,145 g/l, iron (II) — 0,558 g/l, aluminium (III) — 2,351 g/l and silicon (IV) — 0,065 g/l, as follows. Aqueous and organic phase (15% DEHPA and 85% kerosene) were contacted at ratio of 1,25, which was found out to be the best in the range between 1, 1,25 and 1,5, by moving the turbine impeller after the addition of a measured volume of alkali (1 M NaOH) to adjust pH. The phases were equilibrated at an agitation speed of 650 rev/min, in 30 min (taken according the late experiments); the settling time generally varied between 2 and 5 min. The results, given in Figure 2, show that the highest percentage of iron (III) extraction is reached at pH value of 2,5. Also, the results show that iron (III) is preferentially extracted as the extraction approaches 100 per cent, appreciable amount of iron (II) and aluminium (III) are co-extracted with the iron (III), whereas silicon (IV) is not co-extracted.

The variations with pH of the separation factors (defined as the ratio of the distribution coefficient of iron (III) and iron (II), also iron (III) and aluminium (III), is given in Table I).

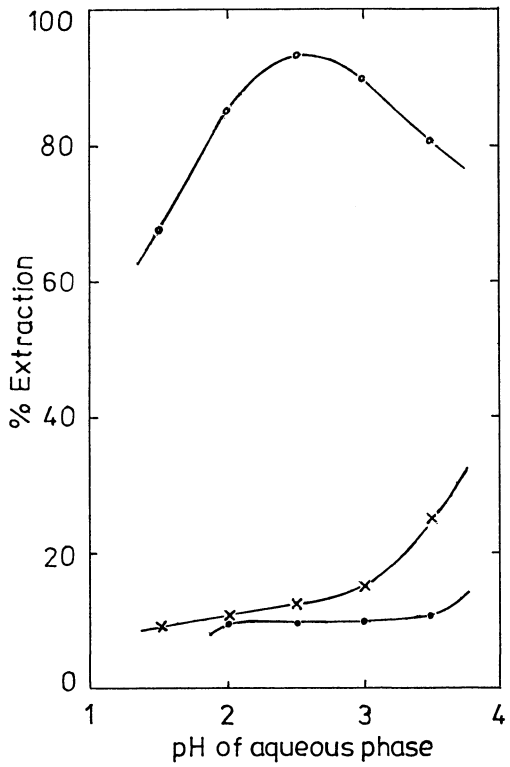

Fig. 2. — Effect of pH value on extraction of iron (III) in the presence of iron (II) and aluminium (III)

o iron (III); ● iron (II); × aluminium (III)

TABLE I

Effect of pH on Iron (III) - Iron (II), Also Iron (III) Aluminium (III) Separation Factor

pH	*Separation factor*	
	$D_{Fe\ (III)}/D_{Fe\ (II)}$	$D_{Fe\ (III)}/D_{Al\ (III)}$
1,5	—	24
2,0	54	48
2,5	113	92
3,0	83	51

3.2. **Dependence of Extraction on Aqueous Iron (III) concentration**

Tests with various aqueous iron (III) concentration values were carried out by changing the aqueous iron (III) concentration diluting the sulphuric acid solution in the range between 0,625 g/l and 2,03 g/l, while the pH value was held the same by 6 M sodium hydroxide, according to the late examination results. Other examination conditions being unchanged.

The results are shown in Table II.

TABLE II

Dependence of Extraction on Aqueous Iron (III) Concentration

Initial Fe (III) concn., g/l	*Equilibrium concentration, g/l*		*Distribution coefficient*
	Aqueous phase	*Organic phase*	
	Fe (III)	*Fe (III)*	
0,625	0,055	0,750	13,636
1,142	0,084	1,322	15,738
1,655	0,087	2,140	24,598
2,030	0,096	2,417	25,177

A very limited fact of the Table II shows that the distribution coefficient increases when changing the aqueous phase concentration of iron (III), the highest being in the range of the examined iron (III) concentration values at the value of 2,030 g/l. It also shows that the distribution coefficient increasing decreases when approaching higher aqueous iron (III) concentration values.

3.3. Dependence of Iron (III) Extraction on DEHPA Concentration

Tests with different concentration of DEHPA in kerosene were carried out by holding two values always the same: the pH value — 2,5 and the aqueous iron (III) concentration value — 2,030 g/l, and organic phase was constituted by changing a percentage of DEHPA in the range between 10 and 25%, while, as the difference to 100%, kerosene was also changed.

The pH change in the course of extraction was also examined. Other examination conditions remained unchanged.

The results are given in Table III and they show that the iron (III) distribution coefficient increases with the increasing of the DEHPA organic solution percentage, while the pH value change follows the change of the extraction. The results also show that the phase equilibrium was obtained in 15 min with the 25% DEHPA organic solution. The

TABLE III

Dependence of Iron (III) Extraction on DEHPA Concentration

DEHPA (%)	*Equilibrium pH*	*Equilibrium concentration, g/l*		*Distribution coefficient*
		Aqueous phase	*Organic phase*	
		Fe (III)	*Fe (III)*	
10	1,80	0,110	2,400	21,818
15	1,75	0,096	2,417	25,277
20	1,71	0,055	2,469	44,891
	1,70*	0,028	2,502	89,357
25				
	1,70	0,028	2,502	89,357

* Mixing time 15 min.

result of the iron (III) extraction also results of the co-extraction of iron (II) and aluminium (III), from the given sulphuric acid solutions, under the optimal conditions found out in the course of the examination, are shown in Table IV.

TABLE IV

Extraction of Iron (III) and Co-extraction of Iron (II) and Aluminium (III) under Optimal Conditions

Initial metal concen., g/l			*Distribution coefficient*			*% Extracted*			*Separation factor*	
Fe(III)	*Fe(II)*	*Al(III)*	$D_{Fe(III)}$	$D_{Fe(II)}$	$D_{Al(III)}$	*Fe(III)*	*Fe(II)*	*Al(III)*	$D_{Fe(III)}/D_{Fe(II)}$	$D_{Fe(III)}/D_{Al(III)}$
2,030	0,989	4,168	89,357	0,431	0,477	98,620	25,639	27,620	207	107

About 98% of iron (III) was extracted and was accompanied by about 25% iron (II) and 27% aluminium (III).

4. CONCLUSION

The solvent extraction process using DEHPA can be applied for separation of iron (III) from the basic sulphuric acid solution, but the problem of a high iron (II) and aluminium (III) co-extraction should be solved primarily. The arrangement apparatus showed, in the course of the experiments, to be a very convenient one for this sort of examination.

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