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Seham Nagib

Academy of Specific Studies, Worker University, Cairo, Egypt, seham67@hotmail.com

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Stripping of Fe (III) from D2EHPA Using Sulphuric Acid, Hydrochloric Acid, and Reductive Stripping in Vacuum

إسترجاع الحديد الثلاثي Fe (III) من D2EHPA باستخدام حمض الكبريتيك وحمض الهيدروكلوريك وكذلك الإسترجاع تحت تأثير الضغط المنخفض في وجود مادة مختزلة

Seham Nagib

Academy of Specific Studies, Worker University, Cairo, Egypt

المخلص

من المعروف ان ايون الحديد الثلاثي Fe (III) يسهل استخلاصه باستخدام D2EHPA ولكن من الصعب إسترجاعه. ومن المعروف ان الحديد الثنائي Fe (II) اسهل فى الإسترجاع من الحديد الثلاثي Fe (III). لذلك إختزال الحديد الثلاثي إلى الثنائي يمكن ان يحل المشكلة. تم دراسة تأثير الأحماض مثل H_2SO_4 و HCl وكذلك وجود ايون الزنك Zn (II) كمادة مختزلة تحت ضغط منخفض على الإسترجاع ايون الحديد الثلاثي Fe(III). وقد أوضحت النتائج أن استرجاع Fe (III) يزداد مع زيادة تركيز الحمض حتى 10N لحمض الكبريتيك، 5N لحمض الهيدروكلوريك. أما بالنسبة للاسترجاع بالاختزال فقد وصلت النسبة إلى 90% في خطوة واحدة وذلك اعتمادا على نسبة A/O عند ضغط 60 kPa.

Abstract

Whereas, Fe (III) is easily extracted using di (2-ethylhexyl) phosphoric acid (D2EHPA), it is hard to strip it from the organic phase. It is well known that Fe (II) is readily stripped from D2EHPA, so a reduction of ferric to ferrous iron could be away to solve this problem. In this work, the conventional way of stripping using acidic solutions such as H_2SO_4 and HCl has been studied. Fe (III) stripping was found to increase with increasing acid concentration. The optimum acid concentration required is 10 N and 5 N for H_2SO_4 and HCl, respectively. Also, reductive stripping in vacuum has been studied by using SHG zinc powder as reducing agent. The optimisation of operating conditions, such as degree of vacuum, acid concentration and quantity of added zinc, has been made. The experiments showed that a stripping yield greater than 90% in only one stage can be achieved, depending on A/O ratio, at 60 kPa of pressure. Iron reduction and stripping have been done simultaneously.

Key words: Iron stripping; D2EHPA; galvanic stripping; reductive stripping.

1- Introduction

Several investigations have been performed to strip Fe (III) from D2EHPA. The common way to extract iron from the organic solvent is by using concentrated acidic solutions, such as H_2SO_4 and HCl [Sahu and Das, 1997, Hirato et al, 1992, Yu Shuqiu and Chen Jiayong, 1989]. The stripping of Fe (III) has been found to increase with increasing H_2SO_4 acid concentration

To increase the Fe (III) stripping from D2EHPA, NH_4HF_2 solution has been used, but the whole process appears to involve many operational steps [Watanabe et al, 1986]. An attempt has also been made to add another organic reagent, such as tributyl phosphate (TBP) [Sahu and Das, 1997], trialkyl phosphine oxide (TRPO) and primary amine N-1923, to the organic phase for the purpose of improving the Fe (III) stripping operation [Chen et al, 1992].

The reductive stripping of Fe (III) is achieved by gaseous reductants, such as SO_2 [Majima et al, 1985] and H_2 [Demopoulos and Gefvert, 1984], but these methods have some feasibility problems due to the high pressure and temperature used.

Over the past few years, galvanic stripping has been studied: this method is based on the ability of a solid metal (Zn or Fe) to directly reduce ferric iron to the ferrous state in an organic medium [Lupi and Pilone, 2000,

Chia et al, 1994, Belew et al, 1993, and Moats and O'keefe, 1996]; some tests have been carried out by using nitrogen, either bubbled through the liquid or introduced above the liquid level in the vessel [Belew et al, 1993, Lupi and Pilone, 2000].

In this work, the ferric ion stripping from D2EHPA was carried out using acidic solutions such as HCl and H_2SO_4 , and by galvanic stripping using Zn powder as the reducing agent in vacuum. The redox reaction in the organic phase and the stripping were simultaneously performed in a stirred flask at different degrees of vacuum.

2- Experimental

2.1 Reagents

Highly purified D2EHPA was kindly donated by Daihachi Chemical Co. Ltd. and was used as received without any further purification. Reagent grade kerosene was used as a diluent. The D2EHPA concentration was measured by means of acid-base titration method using KOH dissolved in ethanol as a base reagent.

2.2 Method

2.2.1 Loading

A 26 mM solution of D2EHPA in kerosene was used. The Fe (III)-loaded D2EHPA was obtained by mixing ($A/O=1$, $[Fe]=0.4 \text{ Kg/ m}^3$) the organic solution with reagent grade $FeCl_3$ aqueous solution. The concentration of the metal

ion in the organic phase was calculated from the difference between the metal ion concentration in the aqueous phase before and after loading.

2.2.2 Stripping

In the case of stripping using acidic solution, the loaded organic was contacted for 5 min at room temperature with H_2SO_4 / HCl solutions and the strip solution was diluted to the required level for iron analysis.

On the other hand, in the case of galvanic stripping, carried out at room temperature, a vacuum flask was used: the vacuum was achieved using a water ejector joined to the flask by a vacuum pipe, with a pressure gauge to measure the degree of vacuum.

At the beginning of each galvanic stripping experiment, the two phases, the Fe (III)-loaded D2EHPA (50 mL) and the H_2SO_4 aqueous solution (50 mL), were put into the flask; subsequently, a weighed amounts of SHG zinc powder was added as the reducing agent and the flask was sealed with a rubber band. The mixture was continuously stirred by a magnetic stirrer. At the end of each experiment, the vacuum was maintained until the two phases had become separated. After each test, the aqueous was analysed by AAS.

3- Results and Discussion

3.1 Iron Extraction

Fig. 1 shows the extraction isotherm for Fe(III) with D2EHPA

3.2 Acidic stripping

Sufficient quantity of the loaded organic with 0.40 kg/m^3 of iron was prepared under the above conditions and iron stripping was studied using both H_2SO_4 and HCl (of different concentrations). From Fig.2, it can be observed that in both cases, stripping increase up to a certain level and then decreases. The decrease in stripping is more pronounced in case of HCl. About 88 and 99 % iron stripping takes place with 10 N H_2SO_4 and 5 N HCl, respectively in a single stage at the A/O phase ratio of 1:1. But, the use of a concentrated acidic solution such as 6 M HCl can degrade the organic phase [Sahu and Das, 1997, Hirato et al, 1992].

3.3 Galvanic stripping

3.3.1 Effect of time

Testing of the required time to reach the maximum yield of iron stripping in vacuum was carried out. These experiments were performed using A/O phase ratio of 1:1 of the aqueous containing $0.045 \text{ M } H_2SO_4$. The reducing agent was Zn powder, whose quantity was four times the stoichiometric one, to promote the Fe (III) ion reduction. A pressure of 15 kPa was chosen in vacuum tests to ensure a

sufficiently low P_{O_2} ; this value is a compromise between two opposite needs: to avoid iron re-oxidation and to have low energy consumption.

Fig. 3 shows the stripping yields as a function of operating time. The stripping yield in vacuum rapidly rises in the first 10 min, reaches the maximum value at 40 min and remains constant for longer times. The subsequent tests were therefore carried out in vacuum with a fixed 40 min contact time.

3.3.2 Effect of Zn amount

In Fig. 4 the iron stripping (%) is reported as a function of the percent Zn excess (E):

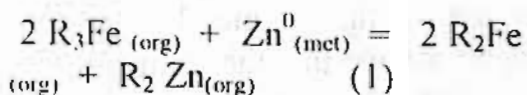
$$E = [(Zn_u - Zn_{st}) / Zn_{st}] 100$$

Where Zn_u is the zinc amount used and Zn_{st} (0.15 g) is the stoichiometric amount.

It can be seen that the amount of stripped Fe increases up to $E = 250\%$, after this value, it shows no variations. In this test, the amounts of Zn in both organic and aqueous phase were measured (Table 1).

Table 1 highlight that the dissolved zinc in the organic phase becomes higher on increasing the added powder amount, although the Fe (III) initial concentration in this phase is the same. Observing the data of Fig. 4 and Table 1, it is evident that the zinc in the organic phase is always higher than the

stoichiometric amount needed for the redox reaction:



It can be said that by adding more than four times the stoichiometric quantity of Zn, the iron stripping yield remains almost constant although the Zn dissolved in the organic phase increases. This observation suggests that a part of zinc powder dissolves in the organic phase since the aqueous phase equilibrium pH (about 1) is too low to have a considerable extraction of Zn by D2EHPA. As can be observed in Table 1, the Zn concentration in the aqueous solution is practically constant, whatever the Zn powder amount may be.

In the following experiments, the excess of Zn powder added was maintained at 250 %.

3.3.3 Effect of stripping solution acidity

To establish the influence of the stripping solution acidity on the iron stripping yield, the concentration of H_2SO_4 was varied in the range 0.045 – 0.25 M, maintaining the pressure at 15 kPa; Fig. 5 shows the results obtained during these experiments. The iron extraction yield increases with increasing H_2SO_4 concentration up to 0.12 M, and then, no significant increases of extraction are

observed. The dissolved Zn, that is about 45 % of the added metallic powder, is shared between the aqueous and organic phases, depending on acid concentration. The Zn concentration in the aqueous phase increases with increasing solution acidity, while the Zn present in the organic phase shows an opposite trend. On the basis of the data reported in Fig. 5, it is possible to observe that the Zn dissolved is around 60 % higher than the stoichiometric amount required for the iron reduction, showing once again that another reaction is involved. In order to perform in the same operation, both iron reduction and stripping with high extraction yield, the 0.1 M H₂SO₄ aqueous solution has been used, thus, minimizing the Zn losses in the aqueous phase. The Zn dissolved in the organic phase can be subsequently recovered in the stripping stage.

3.3.4 Effect of pressure

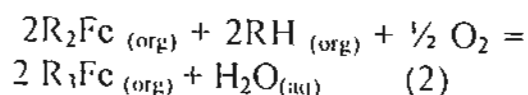
The influence of pressure on the process was investigated at fixed reaction time, Zn powder amount, and H₂SO₄ concentration.

In Fig. 6 the iron stripping yield and the Zn dissolved in both phases are reported as a function of the pressure.

Fig. 6 shows that iron extraction yield remains constant from 15 to 75 kPa and rapidly decreases at near atmospheric pressure: this

result indicates that the reduction of Fe (III) and the consequent stripping of Fe (II) are favoured when the pressure is lower than atmospheric. To obtain an iron stripping yield greater than 90 %, a pressure no higher than 75 kPa is required.

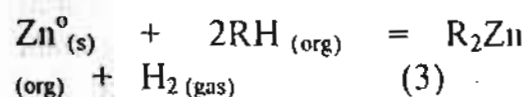
The Zn in both phases could be considered constant up to 60 kPa, thus, indicating the same trend of iron; with the pressure increasing, the Zn dissolved in the organic and aqueous phase rises slightly. This behaviour can be explained, considering that when the P_{O_2} rises, the following reaction is involved:



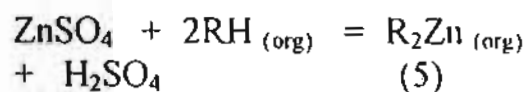
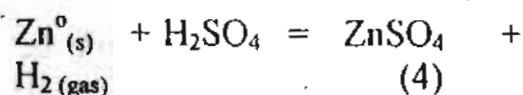
But up to 75 kPa, the reduced iron remains the same and this means that larger amounts of Zn are engaged in the reduction (reaction (1)); above this pressure, reaction (2) prevails over reaction (1). The Zn in the aqueous phase increases with pressure because Zn dissolution is favoured by P_{O_2} increase, but it cannot be extracted that at low pH, Zn could be partially stripped from organic phase.

In all the experiments the Zn amount in the D2EHPA was noticed to be greater than the quantity required to reduce iron, so another reaction occurs as previously said, probably the direct dissolution of the solid Zn

in the organic phase, according to the reaction:



Rather than:



Though the Zn is one of the most extractable metals by D2EHPA, reaction (5) cannot occur significantly at the considered pH.

Conclusions

1. Acidic stripping

Stripping studies of iron loaded on to D2EHPA (~ 0.40 kg/m³) was carried out using H₂SO₄ and HCl. It is observed that stripping increases with increasing acid concentration up to 5 N HCl and 10 N H₂SO₄ and then decreases with further increases in acid concentration. However, the decreasing is more with HCl.

2. Vacuum stripping

The stripping behaviour of Fe (III) from D2EHPA at various degrees of vacuum, with an H₂SO₄ aqueous solution adding metallic zinc powder as reductant, was studied. Several tests were performed in order to

investigate the effect of contact time, added quantity of Zn powder, H₂SO₄ concentration in aqueous solution, and vacuum degree on iron stripping yield.

The results showed that:

- Contact time of 40 min is required to reach the maximum yield;
- A Zn excess of 250% compared with the stoichiometric quantity gives satisfactory results;
- Though the acidity of aqueous solution improves the iron stripping, high H₂SO₄ concentration could not be used because of large Zn losses;
- 75 kPa pressure allows us to obtain the same iron extraction yield achieved at lower pressure, but the Zn dissolved at 75 kPa is higher than that dissolved at 60 kPa.

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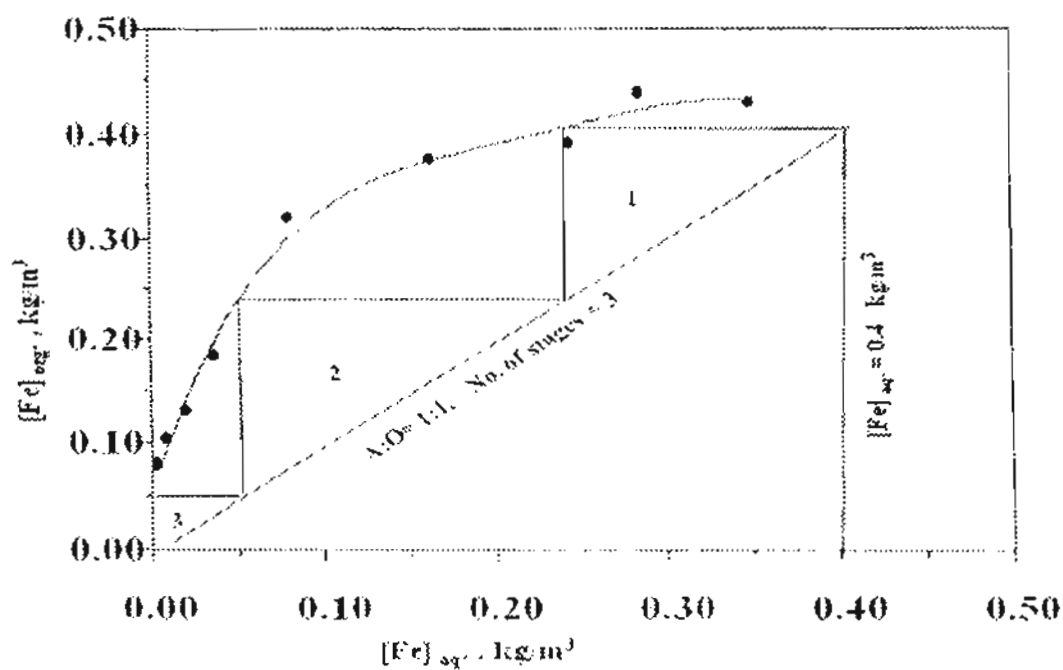
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Table 1: The relation between the amounts of add Zn powder and Zn distribution into the two phases.

Zn powder (g)	Zn organic (g/L)	Zn aqueous (mg/L)
0.15	1.33	0
0.25	1.69	50
0.35	2.15	80
0.55	2.56	63
0.75	3.00	45
2.00	8.52	68



[HCl] = 0.55 N, [Fe]_{aq} = 0.4 kg/m³, [D2EHPA]_{org} = 20 mM

Fig. 1: Extraction isotherm for Fe(III) with D2EHPA.

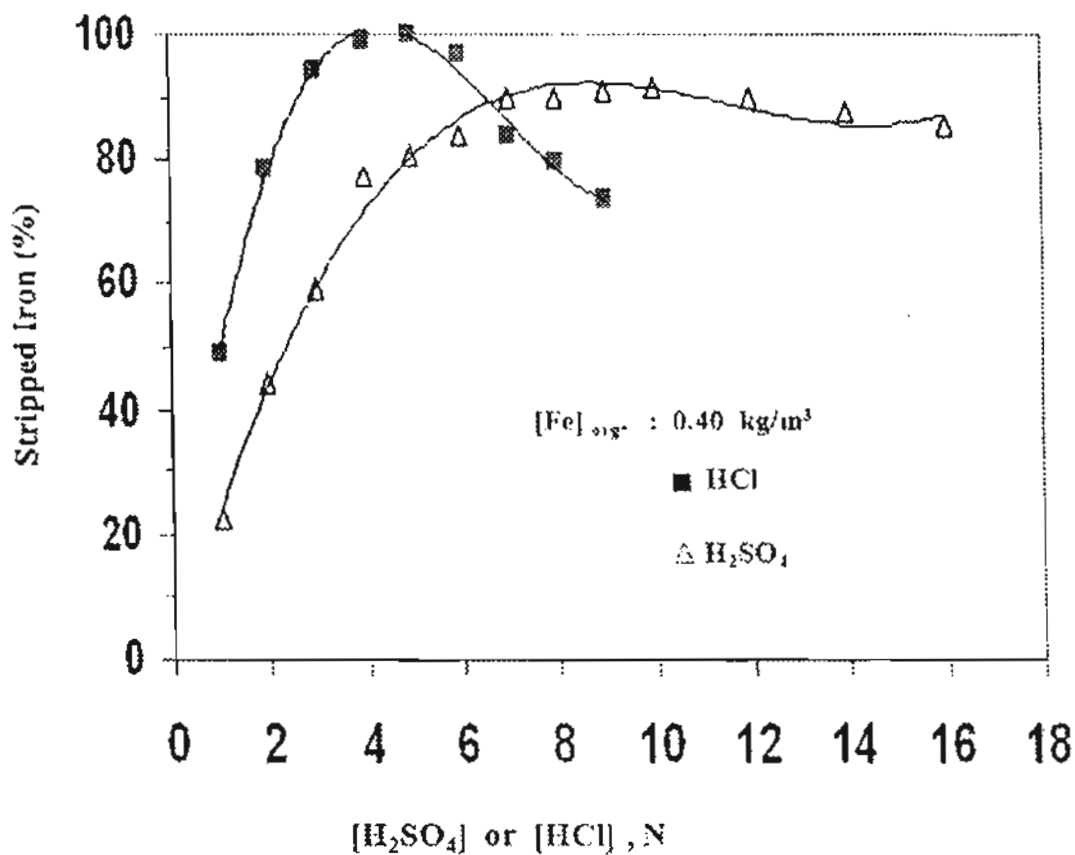
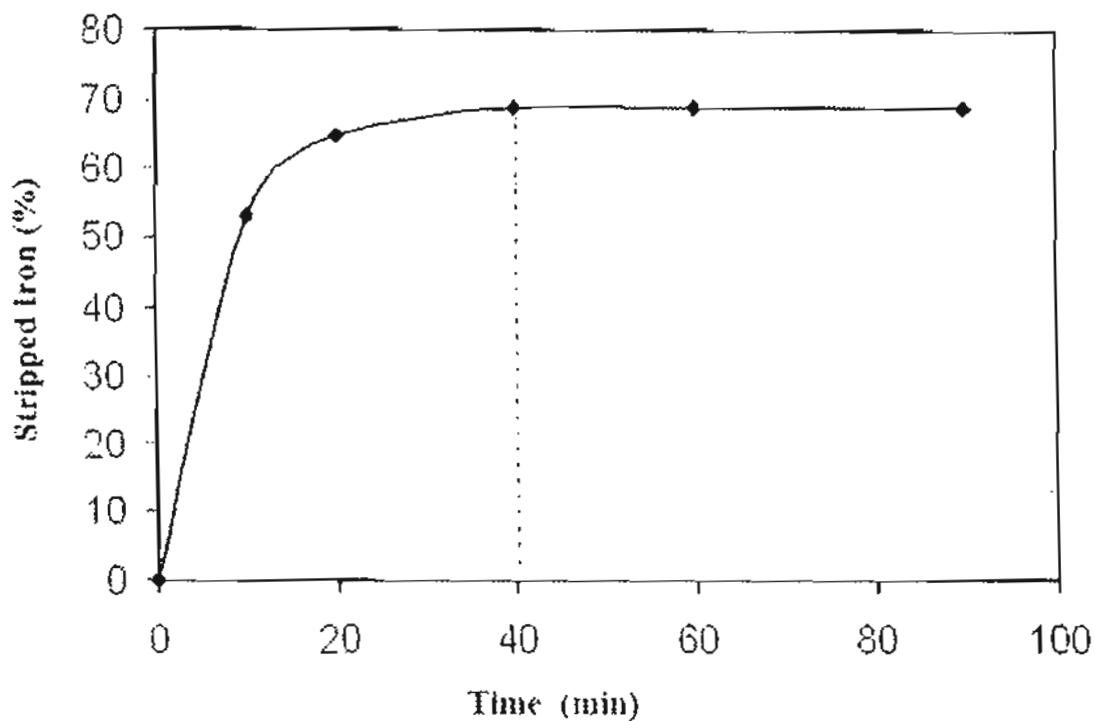
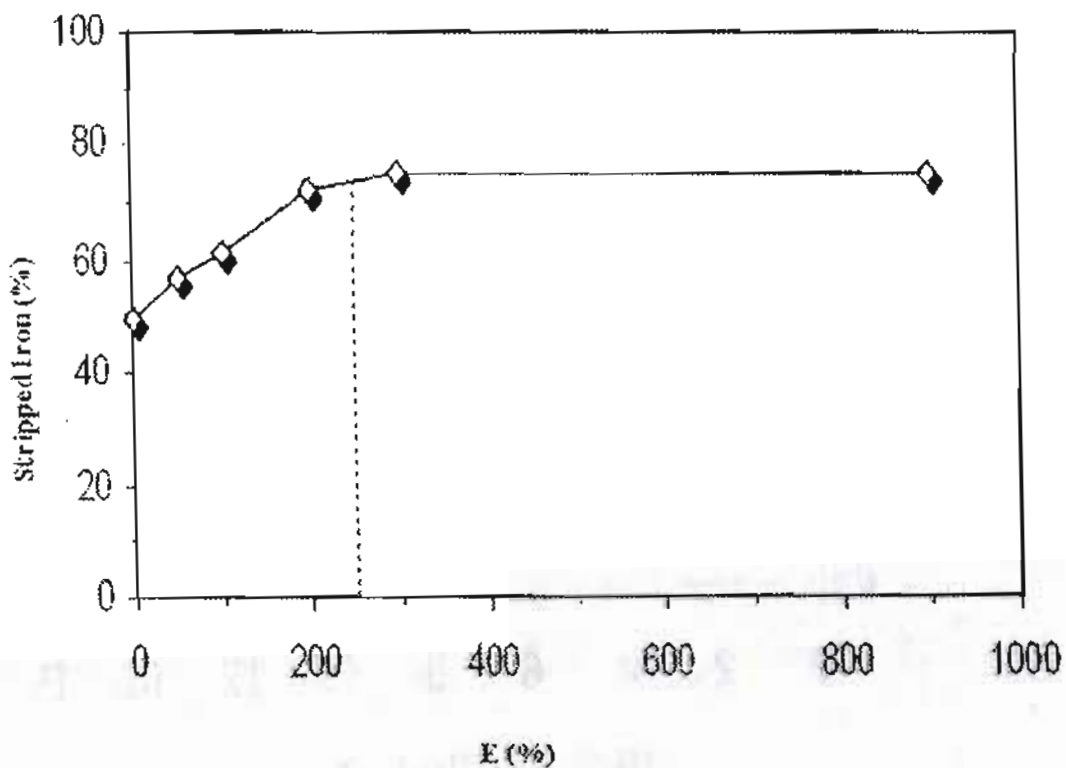


Fig. 2: Effect of H₂SO₄ and HCl normality on iron stripping from loaded D2EHPA.



15 kPa, 0.045 M H_2SO_4 and using excess of Zn

Fig. 3: Effect of time on iron stripping percentage.



15 kPa, 0.045 M H_2SO_4

Fig. 4: Effect of E% on iron stripping percentage.

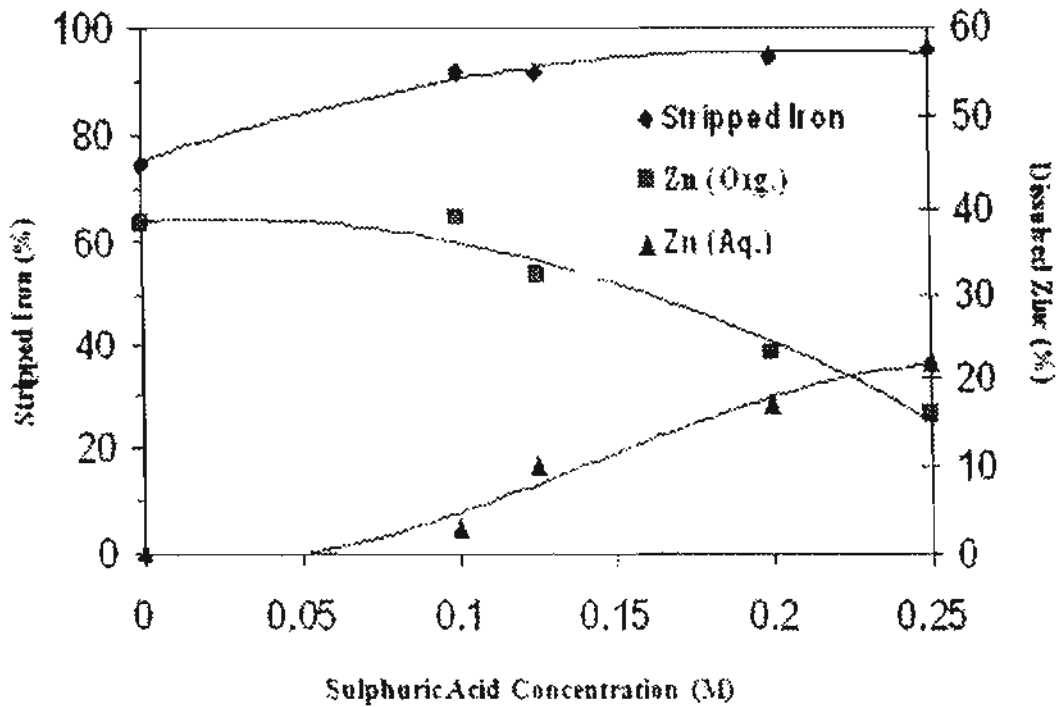
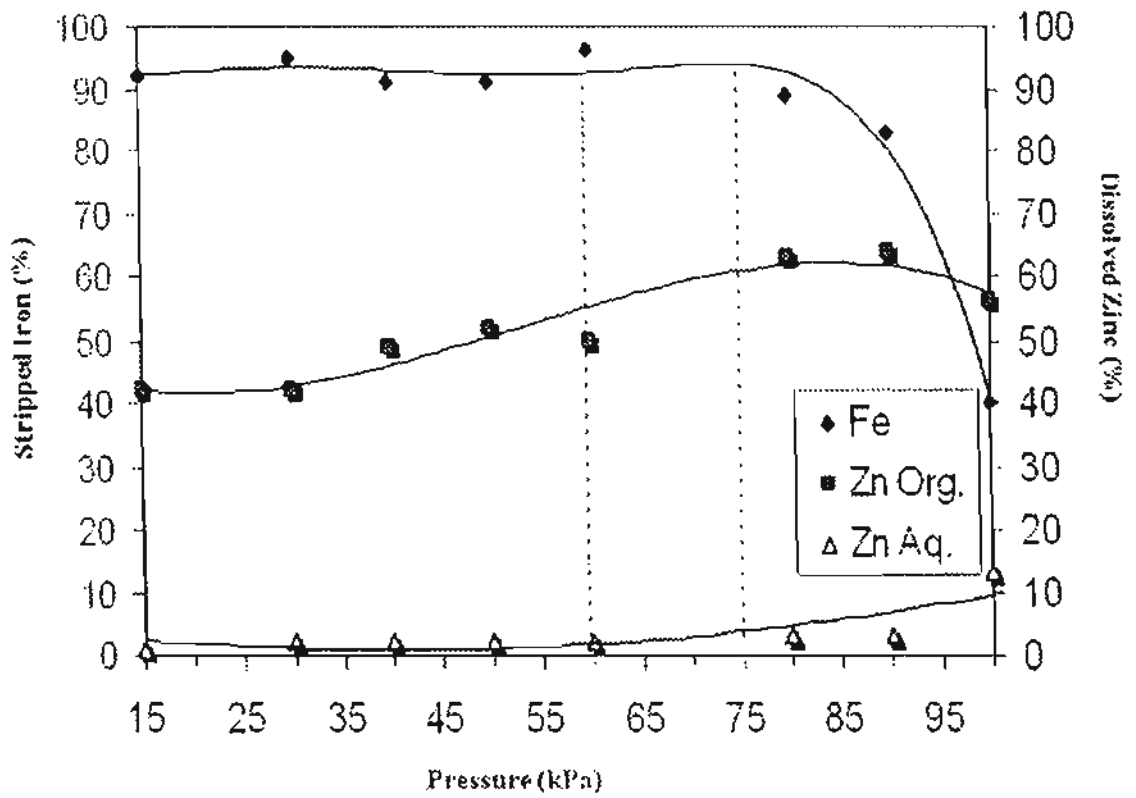


Fig. 5: Iron stripping yield and amount of zinc dissolved vs. acidity of stripping solution.



Time 60 min, E: 250 % and 0.1 M H₂SO₄

Fig. 6: Effect of pressure on iron stripping and dissolved zinc.