AMERICAN JOURNAL OF PHARMTECH RESEARCH

Journal home page: http://www.ajptr.com/

Determination of Iron in Ferrochrome slag – A Solvent Extraction study

A.V.L.N.S.H.Hariharan[1*] Ch. Sudhakar[1], B.Venkateswara Rao[2]

1 Department of Chemistry, GIT, GITAM University. Visakhapatnam – 530 045,India.

2 Department of Engineering Chemistry, Andhra University. Visakhapatnam – 530 045,India.

ABSTRACT

Solvent extraction of iron (III) from hydrochloric, sulphuric, nitric and perchloric acid solutions with Tri-n-butylamine (TBuA) in benzene has been studied. The extractions are nearly quantitative from all the acid solutions. The optimum conditions for extraction were established from the study of the effect of several variables like concentration of amine, metal ion, acidity, foreign ions etc. Attempts are also made to strip iron from the organic phase with 1.0M H_2SO_4. The extracted species are identified. The method has been applied for the determination of iron in tap water as well as ferrochrome slag.

Keywords: Solvent extraction -iron (III) - Mineral acid - Tri-n- Butyl amine [TBuA] - Slag

*Corresponding Author Email: ahharan@gmail.com

Received 17 October 2013, Accepted 28 October 2013

Please cite this article in press as: Hariharan AV. *et al.*, Determination of Iron in Ferrochrome slag – A Solvent Extraction study. American Journal of PharmTech Research 2013.

INTRODUCTION

Extraction of iron (III) from aqueous hydrochloric[1-4] sulphuric[5,6] nitric, citric[7], perchloric[8] and other acid solutions[9] has been reported by earlier workers by different reagents. It is an observed fact that the free amine cannot extract iron (III) from aqueous acid solutions. The object of the present study aims at the extraction of iron (III) by Tri-n-butyl amine (TBuA) from hydrochloric, sulphuric, perchloric and nitric acid solutions and to establish the nature of the extracted species.

The solid material obtained from the interaction of flux and impurities in the smelting and refining of metals is termed as slag. The solid product in the silicate glass material is of non-metallic nature[10]. The byproducts of coal burning and combustion processes generates bottom ash or fly ash .Smelting of ores of copper , zinc, lead etc results in the formation of metal slag in base metal industry. These have high concentrations of heavy metals embedded in glass matrix or solid surface[11.] Ferro alloys such as Ferrochrome are generally produced by electronic arc furnace from melting of mineral chromites[12]. These are the sources for the production of all types of steels with different alloying metals (nickel, molybdenum, vanadium etc.) making the steel more passive and increasing its stainless steel properties[13]. The slag that is generated consists of oxides of magnesium, iron and chromium of various oxidation states. The slag may contain chromium in +3 and +6 oxidation states along with elemental chromium[14].

The slag sample in the present investigation is a composite from Jindal Ferro Alloys Corporation, Kothavalasa, Visakhapatnam Dt. The chemical composition of the slag is Cr_2O_3-10-15 %, FeO-2-5 %, SiO_2-25 – 30 %, MgO-22-25 %, Al_2O_3 16-22% and CaO-3-5%

In the present work, attempts were made for the analysis of iron in tap water as well as ferrochrome slag.

MATERIALS AND METHODS

Experimental:

A 0.5 M TBuA (Mol. Wt. 185.35gm/ml) in benzene was prepared and diluted appropriately to get the required concentration. Ferric (E.Merck) (Mol.Wt.270.3 g/mol) was used for preparing iron (III) solution (0.45M) and was standardized using standard potassium dichromate solution volumetrically. Double distilled water was use throughout the studies. All other chemicals used were of Anala R grade and are purified by standard methods.

Iron (III) Extraction Procedure

An aliquat (10ml) of iron (III) of appropriate concentration and mineral acid were equilibrated with an equal volume of TBuA in benzene (0.05M)[pre-equilibrated with 0.1M mineral acid]

was shaken for 5 minutes. The two phases were allowed to settle and were separated .Iron(III) from the organic phase was stripped with 10ml of 1.0M H_2SO_4 and was estimated spectrophotometrically[15] by measuring the absorption of Fe(III) – thiocyanate complex at 480nm, using Shimadzu UV-Visible Spectrophotometer type UV-260. The equilibrium iron (III) concentration in the organic phase was determined by taking the difference in the initial and the equilibrium iron (III) concentrations in the aqueous phase.

Determination of iron (III)

i) Tap Water

The proposed method was applied to the determination of iron(III) in tap water using AAS model-SVL Spectronics – 205. The samples were filtered through a membrane filter (with pore size 0.45 µm) immediately after sampling and are acidified with hydrochloric acid to about pH 2 for storage. An aqueous solution (10ml) of iron (III) has been equilibrated with an equal volume of TOA (0.05 M) in benzene pre equilibrated with appropriate concentration of hydrochloric acid. The iron (III) concentration in the aqueous phase before and after extraction was estimated as described above.

ii) Slag sample

About 1.0-2.0 gms of slag is dissolved in a mixture of conc. HNO_3 and conc. HCl which is subjected to prolonged boiling and evaporation on a water bath. It is then diluted, filtered (The filtrate is discarded) and washed with distilled water. It is diluted up to 100 ml. An aqueous solution (10ml) of iron (III) has been extracted and estimated as described above.

Effect of stripping agents:

After extraction, iron (III) was stripped with 20ml reagents of various concentrations (0.1 – 2.0 M) of ACOH, H_2SO_4 and NaOH solutions.. It was observed that 1.0 M H_2SO_4 alone is a good stripping agent. However in no case the acid strips out all the iron (III) in a single extraction. 99.8% iron (III) could be recovered from organic phase by making contact three times with equal volumes of 1.0 M H_2SO_4.

RESULTS AND DISCUSSION:

In the extraction of iron (III) by TBuA in benzene as a function of acidity, the distribution ratio (K_d) was found to increase with increase in acid concentration with all the acid systems studied. Maximum extraction efficiency at 9.0 M acidity in hydrochloric and nitric acid media where as in case of sulphuric (8.0M) and perchloric (7.0M) acid solutions is noticed (Fig.1). The extractions are nearly quantitative with both hydrochloric and sulphuric acid solutions.

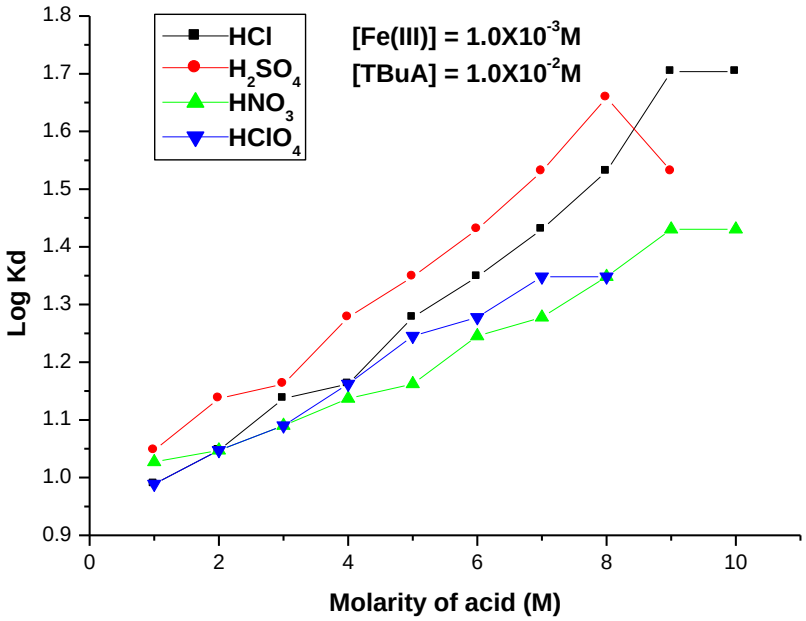

Figure 1: Effect of acidity on extraction

Composition of the extracted species:

In the extraction isotherm method[16] the limiting ratio of the metal to TBuA was found to be unity (1 mole of TBuA=1 mole of Fe(III)) with all the acid systems(Fig-2). The log-log plots of K_d Vs. TBuA in the distribution ratio method[17] gave straight lines. With hydrochloric, perchloric and nitric acid solutions the log-log plot gave straight line of unit slope (Fig-3). On the other hand, the slope analysis of the distribution data in sulphuric acid solutions indicates that the solvation number is two.

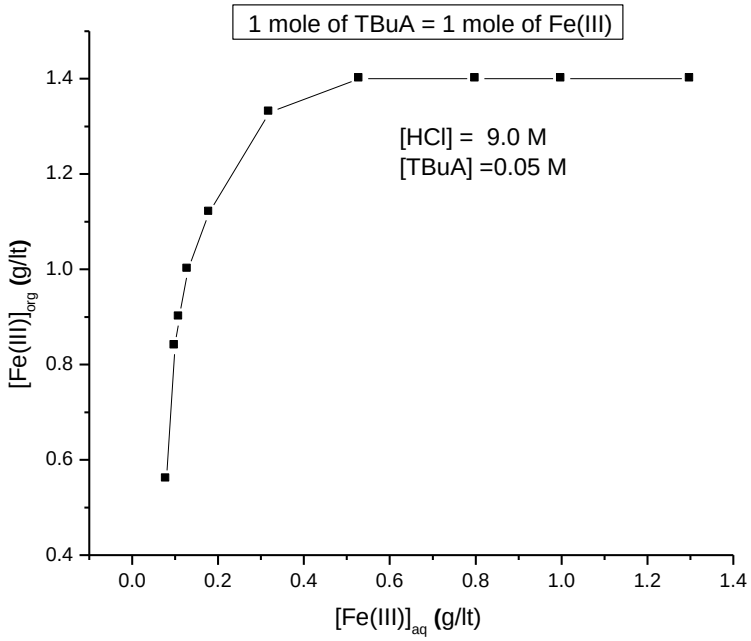

Figure 2: Extraction Isotherm

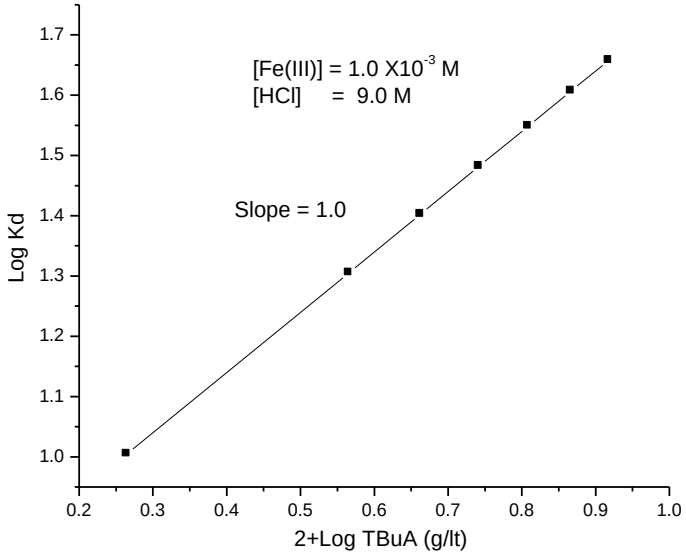

Figure 3: Composition of extracted species

Absorption spectra:

The absorption spectra (U.V. region) from sulphuric acid media exhibits absorption bands[18] at 295 and 355 nm . These two are the absorption characteristics of Fe(OH) and hydroxyl – group bridging species $Fe(OH)_2$ Fe respectively, and the appearance of new peak at 305 nm corresponds to the complexes $FeSO_4^+$ and $Fe(SO_4)^{-2}$.

The observed iron: TBuA molar ratio of unity from solutions (by distribution ratio method) could be explained as arising from the extraction of iron (III) by the following ion-exchange mechanism. According to Smulek , the extracted species in hydrochloric acid is $FeCl_4^-$ which associates with one amine cation to form an ion – pair.

From hydrochloric and nitric acid solutions:

$$TBuAHCl + Fe^{3+} + 4Cl^- \longleftrightarrow [TBuAH^+ FeCl_4^-]_{org} + Cl^-$$

$$TBuAHNO_3 + Fe^{3+} + 4NO_3^- \longleftrightarrow [TBuAH^+ Fe(NO_3)_4^-]_{org} + NO_3^-$$

$$TBuAHClO_4 + Fe^{3+} + 4ClO_4^- \longleftrightarrow [TBuAH^+ Fe(ClO_4)_4^-]_{org} + NO_3^-$$

From sulphuric acid solutions:

$$2(TBuA)_2SO_4 + 2Fe^{3+} + 2SO_4^{2-} + 2H_2O_{(aq)} \longleftrightarrow [(TBuAH)_2SO_4.FeOH(SO_4)_2]_{2\,org} + 2H^+$$

On the basis of the proposed mechanism for the extraction of iron (III), the dependence of the distribution ratio on the nature of the mineral acid.

The results obtained in the proposed method for the extraction of iron (III) was applied to analyze water samples were compared with AAS method. It was observed that these two were in good agreement with each other (Table-1)

Table-1: Analysis of iron (III) in tap water

S.No.	volume of water sample (ml)	Current method	AAS method
1	50	22.0	21.6
	100	26.0	25.7
2	100	58.0	57.2
	200	62.0	61.8
3	100	25.5	24.5
	200	19.5	19.1

Variation of distribution of iron(III) (in the case of slag sample) as a function of aqueous phase concentration of hydrochloric acid are presented in Table-2. The distribution ratio (Kd) increased with increasing concentration of the acid up to 7.0 M and remained constant up to 8.0 M acidity. Quantitative dissolution of iron increases during the first 10 min, followed by gradual decrease after 15-30 min and slowly after 90 min.

$2FeO.SiO_2 + 2HCl \rightarrow 2FeCl_2 + H_4SiO_4$ (1)

Table-2: Variation of acidity with extraction

Molarity of HCl (M)	% of Iron(III) Extracted
0.5	76.38
1.0	88.54
1.5	93.92
2.0	98.20
2.5	98.93
3.0	99.23
4.0	99.36
4.5	99.38
5.0	99.50
5.5	99.62
6.0	99.87
7.0	99.81
8.0	99.81

Oxidation of iron in leaching sample and its dissolution has been done as per the following equations 2 and 3.

$FeO + HCl \rightarrow FeCl_2 + H_2O$ (2)

$2FeCl_2 + H_2O_2 + 2H_2O \rightarrow 2FeOOH + 2HCl$ (3)

Analysis of Fe-Cr alloy recovery (g/kg) was presented in Table-3. The values obtained in this study are compared with those values mentioned as per the certified specifications.

Table-3: Analysis of Fe Cr alloy recovery-(g/kg)

Analyte	Certified	Measured	Recovery (%)
Ca	-----		---------
Cr	680.0	665.0	97.8
Fe	249.8	247.5	99.08
Mg	16.0	15.5	96.9

CONCLUSIONS

The extraction method developed was applied to separate and determine iron in water and slag samples. The % recovery of iron in presence of other metals was found to be 99.08% and the determination can be achieved efficiently in minimum amount of time.

ACKNOWLEDGEMENTS:

Thanks are due to Dr. V. Muralidhara Rao, Retd. Professor, School of Chemistry, Andhra University, Visakhapatnam for his valuable suggestions. Thanks are also due to Principal, GIT and Management of GITAM University for providing necessary facilities to carry out these investigations.

REFERENCES

REFERENCES

1. Lee MS, Lee K J. Sepn of Iron by extraction, Hydrometallurgy, 2005; 80:163
2. Sahu KK, Das RP. Mixed Solvent Systems for the Extraction and Stripping of Iron(III) from concentrated acid chloride solutions, Metallurgy. Met. Trans. B, ,2000; 31(B):1169
3. Staszak K, clerpiszewski R, Pochaska K. Equilibrium and rate of iron(III) extraction from chloride solutionsby individual hydrophobic extractants and their mixtures Polish J. Chem. Tech. 2011;13(1): 1-5
4. Oren JJ, Gough KM , Gesser HD. The solvent extraction of Fe(III) from acidic chloride solutions by open cell polyurethane foam sponge (OCPUFS), Can. J. Chem. 1979; 57(15): 2032
5. Alguacil FJ, Amer S. Study of the amine primene 81R sulphate-$Fe_2(SO_4)_3$ extraction equilibrium system at low temperatures, Polyhedron 1986; 5(11): 1755
6. Cattrall RW, West BO. The extraction of iron (III) from aqueous sulphate solutions by di(3,5,5-trimethylhexyl)amine—I: The nature of the extracted species J. Inorg. Nucl. Chem 1966; 28(12)**:** 3035
7. Pratnitskii AI, TabenskayaTV. Zh.Analit.Khim., 1970; 25: 943
8. Nitsu M, Sekine T, Solvent extraction equilibria of acids—II: Extraction of phosphoric acid from various aqueous solutions with tri-n-octylphosphine oxide J. Int. Nuc. Chem. 1976; 38: 1056
9. Hari Haran AVLNSH, Sudhakar Ch, Naidu AS., Solvent Extraction of Iron (III) by Tri-n-Octyl Phosphine Oxide, Intl. J of Chem. and Phrm. Res, 2011;3(4) : 945-950
10. Motz H, Geiseler J., Products of steel slags an opportunity to save natural resources

Waste Mgt. 2001; 21: 285.

11. Mashanyare HP, Guest. RN. ,The recovery of ferrochrome slag at Zimasco, Miner. Eng. 1997;10 :1253.
12. Mehmet E H. Soner A G, Deniz T M, Tumenb F. Hexavalent chromium removal by ferrochromium slagJ. of Hazs. Mat.B126 2005; 176:182
13. Coetzer G, Giesekke EW. Guest. RN, Hexavalent chromium in the recovery of ferrochromium from slag. Can. Metall. Quart., 1997; 36(4): 261-268.
14. Farjadi MH and Azari J Proceedings: Tenth International Ferroalloys Congress; 2004; 1-4
15. Vogel AI. "A Text book of quantitative Inorganic Analysis" 3rd Edition, Longman, London. 1962.
16. Coleman CF, Brown KB, Moore JG, Allen KA. Proc.2nd Intl.Conf., Peaceful uses of Atomic Energy, Geneva, 1958; C.10, Paper 510.
17. Hesford E, Mckay HAC. Trans Faraday Soc., 1958; 54: 573.
18. Jackwerth E. Z. Anal. Chem., 1964; 206: 335.