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SUGGESTED METHOD FOR DISSOLUTION OF EGYPTIAN BEACH ILMENITE

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طريقة مقترحة لإذابة رمال الالمنيت المتواجد بالشواطئ المصرية

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Abstract

Northern Egyptian coast extending from Abu Qir to Rafah has been endowed with some concentrations of heavy economic mineral sand. The concentrations occur mainly along the beaches and coastal dunes. The principal economic heavy minerals are ilmenite, magnetite, garnet, zircon, rutile and monazite. Since ilmenite constitutes about 50% of these economic heavies, and because of its low titanium and high chromium contents. Some problems concerning the marketing of this mineral were encountered. It was recommended to convert ilmenite to marketable product by either physical dressing techniques and/or by chemical processing to synthetic rutile or white pigment.

An ilmenite concentrate of 98% purity was prepared utilizing gravity, magnetic and high-tension separation. The present paper is concerned with preliminary study upon the dissolution of titanium and iron from such ilmenite. Dissolution was carried out using hydrofluoric acid as the main dissolving agent. Different relevant factors affecting acid dissolution have been studied such as acid concentration, contact time, solid/liquid ratio and finally dissolution temperature were performed to achieve optimum conditions for such dissolution. Moreover, various inorganic acids were investigated to dissolve Ti and Fe from Egyptian beach sand ilmenite for comparison.

Introduction

The Egyptian beach heavy mineral sand deposits contain an average ilmenite content of about 50% (Dabbour et.al.1990; Dabbour, 1994, 1995a, 1995b; Bakhit, 1997 and El-Hadry, 1998). Beach ilmenite is composed of different mineralogical varieties due to its derivation from different rock sources. This is actually the reason of its low content of TiO_2 (42-44%) and hence its unmarketable character. Moreover, it is well known that ilmenite is distributed in the strongly, moderately and weakly magnetic fractions which are obtained by the Isodynamic Magnetic Separator. This wide distribution is related to the presence of alteration products and/or various intergrowths, coatings and exsolution features with hematite, magnetite, brookite, leucoxene, rutile and chromian spinel (Boctor;

1966, Mikhail, 1971,Hammoud, 1973 and Dewedar, 1998). Accordingly, the mentioned intricate relationships render the beach ilmenite to a fairly low-grade titanium, high ferric iron and relatively high chromium ore mineral. Ali (1999) after detailed mineralogical and geochemical studies mentioned that it is possible to adopt better a varity of physical methods for isolating different grades of ilmenite for its effective utilization.

Attempts have been made to develop a suitable process to recover titanium from low-grade ilmenite sand. These include separation of Ti (IV) from Fe (III) present in a sulfuric acid leach liquor produced by heating the powder of ilmenite sand in 18M sulfuric acid for more than 48 hours followed by solvent extraction, stripping and precipitation techniques (Islam et al., in Biswas and Mondal, 1987). Alternatively, Mirda and Islam in 1985 (in Biswas and Mondal op.cited) found that ilmenite sand can be dissolved by heating in a mixture of concentrated nitric and sulfuric acids at boiling point for 24-30 hours, but stage–wise digestion is required.

According to Biswas and Mondal (1987), preliminary experiments to dissolve Ti and Fe from Bangladesh ilmenite sand (<130 μm) in various inorganic acids, indicate that only HF is effective. About 81% Ti is dissolved within 5h by 6.4 M HF at boiling point while only 26% Fe is dissolved. Biswas et al (1992) have prepared a pigment grade TiO_2 (99.9 wt%) from HF leach solution by precipitating the Ti and Fe compounds from fluoride leach by NaOH followed by iron oxidation to ferric state and its extraction with methyl isobutyl ketone. This was followed by pH adjustment and Ti extraction by di-2-ethylehexylphosphoric acid. By this process, it would be possible to eliminate harmful transition metals e.g. Cr and Co beside the production of a marketable pure iron product (Fig.1). Hansen et al., (1995) have however investigated Ti and Fe extraction from ilmenite by fluosilicic acid (H_2SiF_6) using 2.6M H_2SiF_6 at 85C, 49% of the Ti and 53% of the Fe were extracted from 44-74 μm NewYork rock ilmenite in 3h.

The present paper would deal with the preparation of a proper ilmenite concentrate from the Egyptian beach sands followed by studying its dissolution behavior in HF acid in comparison to other mineral acids.

Hammoud (1973) on up grading of Egyptian beach sand ilmenite suitable for sulfuric acid process applied roasting, magnetic and electrical separation techniques. Moderately and weakly magnetic ilmenite fractions were chosen for these purposes. The two magnetic fractions represent 88.74% of the bulk ilmenite, so the recovery was relatively low and the product of the leaching process contains 63.3% TiO_2 and 25.5% Fe. On the other hand, Nell and Hoed (1997) were able to separate chromium oxides from low-grade ilmenite of Northern Kwazulu-Natal and Mozambique placer deposits. They attained a TiO_2 recovery of 95% and a desired Cr_2O_3 removal by roasting under oxidizing conditions followed by magnetic separation. In the present work, it was however suggested to produce a bulk ilmenite concentrate regardless the high iron and chromium content and without rejecting the highly iron ilmenite fraction which by HF dissolution method would be considered as an economic target. Different physical processes including screening, wet tabling, magnetic and electrostatic separations were applied to prepare the ilmenite concentrate (Fig.2).

Experimental

Preparation of Ilmenite Concentrate

A technological sample of a bout 500-kg representing the high-grade raw beach sand was properly collected for the preparation of the study ilmenite concentrate. The mineralogical composition of the raw sands sample is shown in Table (1).

Table (1): Mineralogical Composition of Egyptian High Grade Beach Sand

Economic heavy minerals		Gangue minerals	
Mineral	**Weight %**	**Mineral**	**Weight %**
Ilmenite	46.50	Colored + colorless silicate	21.05
Magnetite	18.00	Quartz	6.40
Zircon	3.50		
Garnet	3.00		
Rutile	1.20		
Monazite	0.35		

The collected technological sample was treated by dry screening using a 2mm screen where seashells and other foreign materials are moved. The undersize fraction (-2mm) was then fed to a conventional (Wilfely type) wet shaking table for gravitative concentration where, a concentrate of economic heavy minerals including 98% of input ilmenite was recovered. The concentrate comprises mainly ilmenite, magnetite, garnet, zircon, rutile and monazite. However, the latter was contaminated with some fine-grained gangue minerals (epidote, pyroxenes, amphiboles and quartz) although most of these minerals have been discarded as tailing. The resultant tabling concentrate was dried and subjected to the High

Intensity induced roll Magnetic Separator (Carpco MLT, lift type)) where it was differentiated into three magnetic fractions and a non-magnetic fraction. The objective was to remove magnetite separately and to concentrate ilmenite beside concentrating the rest of the associated economic heavy minerals such as zircon, rutile, monazite and leucoxene in a non magnetic fraction. The products of this process were as follows:

1- A magnetite fraction which was separated at 0.05 A.

2- A highly magnetic ilmenite fraction which was later separated at 0.5A

3- A magnetic fraction separated at 1.10 A., which is mainly a concentrate of ilmenite, associated with some garnet, and other gangue minerals as epidote and amphibole.

4-The non-magnetic fraction at 1.10 A. was mainly composed of monazite, leucoxene, rutile, zircon and some gangue silicate minerals and quartz.

The magnetic fraction separated at 1.1 A. was then subjected to high-tension electrostatic separation. According to Khazback (1972) and Erasmus (1997), ilmenite at 100 to 120°C behaves as a very good conductor and a high-tension roll separator would be suitable for purification of the mineral. Thus; it was possible to eliminate garnet, epidote and amphibole minerals as non-conductors in a mixed field with negative polarity. On the other hand, some traces of discrete chromite grains were eliminated as poor conductors in a static field with positive polarity. Accordingly, it was possible through this flowsheet (Fig.2) to obtain an almost pure ilmenite concentrate assaying up to 98.42% ilmenite with a total recovery of 97.22%. Analysis of the latter showed that iron oxide amounted to 51.1% while titanium dioxide attained 46.29%.

Leaching Procedure

Several leaching experiments were performed upon the prepared ilmenite concentrate. Each experiment was performed by placing a 5-gram sample portion in 250 ml covered teflon beaker with a known volume of the dissolution reagent (HF). The reaction mixture was then stirred for the required time using a magnetic stirrer. At the end of each experiment, a small volume of water was added to the reaction mixture and the slurry was then filtered in a 100-ml plastic-measuring flask. The residue was washed several times with a little amount of water and the filtrate and washings were then made to volume.

Five leaching factors affecting the dissolution of the prepared ilmenite concentrate have been studied to determine the optimum condition for maximum dissolution efficiency. These factors included acid concentration, solid /liquid ratio, agitation time, reaction temperature and finally the type of the acid

(H_2SO_4 and HNO_3) for comparison. The reaction of HF with ilmenite can be represented by the following possible chemical equation:

$$6HF + FeTiO_3 \longrightarrow Fe^{2+} + Ti^{4+} + 6F^{-} + 3\ H_2O.$$

According to this relation, ton ilmenite concentrate would require a bout 0.8 ton HF for complete dissolution.

Analytical Control

Analysis of Ti and Fe was carried out using GBC 932 AA atomic absorption spectrophotometer. Instrumental parameters for iron and titanium analyses were fixed as shown in Table (2).

Table (2) Instrumental Parameters for the Atomic Absorption Analysis of Iron and Titanium.

Element	L.C., mA	W.L. mm	S.W., nm	Flame type
Fe	7.0	372.0	0.2	Air acetylene
Ti	18.0	364.3	0.2	Nitrous oxide-acetylene

Results and Discussion

Effect of Acid Concentration

In order to study the effect of input acid concentration on the dissolution efficiency of both titanium and iron from the study ilmenite concentrate, a series of experiments were performed with HF moularity varying from 2 up to 10 M. The other variables were kept constant at a sand size of −150 mesh, an agitation time of 1h, in a solid /liquid ratio of 1/4 at room temperature. The obtained results are given in Table (3) and the corresponding plot is given in Fig.3.

Table (3): Effect of Acid Concentration (M) upon Titanium and Iron Dissolution Percent of Egyptian Ilmenite Concentrate.

Acid concentration, M	Dissolution Efficiency %	
	Iron	Titanium
2	8.50	9.10
4	21.70	23.60
6	35.60	37.50
8	38.56	39.40
10	39.10	40.20

From the obtained data, it is clear that ilmenite dissolution percent increases with the increase of the acid concentration from 2 to 10 M. This is corresponding to an increase in the iron and titanium dissolution from 8.50 to 39.10 % and from 9.10 to 40.20) respectively. The obtained results are indeed encouraging where a Ti leaching efficiency of about 38% is obtained by 6M HF during only 1hr at ambient temperature. Under the applied experimented conditions, acid input at 6M amounts to 2.4g which could dissolve about 3g of ilmenite concentrate i.e 60% of the input ilmenite. At 10M HF, the acid input increased to almost the required stoichiometric amount and the dissolution efficiency was only about 40% Compared to severe conditions of H_2SO_4 leaching found by the previous mentioned above, HF can be considered a highly promising acid for ilmenite dissolution. Improvement of the obtained leaching efficiency would be achieved by application of high temperature and/or longer leaching time and/or finer grain size. Beside presence of the required acid amount

Effect of Solid /Liquid Ratio

In order to study the effect of solid /liquid ratio (pulp density) upon titanium and iron dissolution efficiency from the study ilmenite concentrate by hydrofluoric acid another series of dissolution experiments was carried out. In this series, the solid /liquid ratio was serially decreased from ½ down to 1/5 at 6M acid concentration while fixing the other leaching conditions; namely grain size, the leaching time and temperature were kept as in the previous leaching series. The obtained data are given in Table (4) and presented in Fig.4.

Table (4): Effect of Solid /Liquid Ratio upon Titanium and Iron Dissolution Percent of Egyptian Ilmenite Concentrate.

Solid/Liquid Ratio	Dissolution Efficiency %	
	Iron	Titanium
1\2	15.33	26.89
1\3	16.95	35.56
1\4	35.60	37.50
1\5	37.90	41.00

The obtained results showed that decreasing the solid/liquid ratios from ½ to 1/5 is associated with an increase in both iron and titanium dissolution efficiency from 15.33 to 37.90% and from 26.89 to 41.00% respectively. This improvement might be due to the increase of the acid amount and/or the solubility product of the formed compounds. Also from, the above data, a slight increase in the leaching efficiency obtained by the latter S/L ¼ and 1/5., was used to study the next two factors of leaching and temperature.

Effect of Agitation Time

For studying the effect of the agitation time upon titanium and iron dissolution efficiency by hydrofluoric acid from the working ilmenite concentrate, a series of dissolution experiments was performed in which the time of agitation was increased from 1 up to 6 h. The obtained results are given in table (5) and their plot is presented in Fig.(5). Other leaching conditions were fixed as mentioned above (6M acid, ¼ for the S/L ratio and ambient temperature).

Table (5): Effect of Agitation Time upon Titanium and Iron Dissolution Percent of Egyptian Ilmenite Concentrate.

Time, h	Dissolution Efficiency%	
	Iron	Titanium
1	35.60	37.50
2	37.50	38.90
3	38.57	40.20
4	38.90	41.45
5	39.40	41.70
6	39.50	42.10

From the obtained data, it is clearly evident that only a rather slight improvement in both titanium and iron dissolution efficiency was achieved (from ~36-42%). Thus only about 4% in leaching efficiency was added by increasing the leaching time from 1 to 6h.

Effect of Temperature

Given the relatively low leaching efficiencies obtained previously, it was found necessary to study the effect of temperature up to the boiling point. Thus, a series of dissolution experiments was carried out at higher than ambient temperature (60°C, 80 and boiling point) while fixing the other dissolution factors (6M acid, ¼ S/L ratio and 1h agitation time. The obtained results are given in Table (6) and their plot is presented in Fig. (6).

Table (6): Effect of Temperature upon Titanium and Iron Dissolution Percent of Egyptian Ilmenite Concentrate.

Temperature, °C	Dissolution Efficiency%	
	Iron	Titanium
Room	35.60	37.50
60	37.30	48.70
80	40.80	75.40
Boiling point (B.P)	44.00	85.60

The obtained data indicated clearly that by raising the pulp temperature from the room temperature to the boiling point, the titanium dissolution efficiency was considerably increased from 37.50 up to 85.60%. On the other hand, the rate of iron dissolution increased only slightly from 35.60 at room temperature to only 44.00 % at the boiling point. The low dissolution efficiency of iron might be due to the relatively low solubility product of its dissolved fluoride. On the other hand, the Ti dissolution efficiency exceeding 85% at the boiling point indicated that the above mentioned possible reaction of ilmenite with HF does not adequately explain the mechanism of the actual reaction.

Type of Acid

Sulfuric and nitric acids as dissolution reagents were chosen for comparative dissolution efficiencies of the studied ilmenite concentrate with that obtained by hydrofluoric acid. In these tests, the previously mentioned fixed working factors were used at the boiling point (6M acid, ¼ for the S/L ratio and for 1h agitation time. The obtained results in shown in Table (7) revealed that HF dissolved 85.6% of the Egyptian ilmenite concentrate while those obtained by H_2SO_4 and HNO_3 attained only 26.9 and 21.10% dissolution efficiency respectively. It is also interesting to refer to the work of Belyakova and Dvernyakova, (in Biswas and Mondal, 1987) who mentioned that ilmenite is only partially leachable with 20% hydrochloric acid under high pressure and temperature.

Table (7): Effect of Acid Type upon Titanium and Iron Dissolution Percent of Egyptian Ilmenite Concentrate

Acid type	Dissolution Efficiency%	
	Iron	Titanium
H_2SO_4	21.50	26.90
HNO_3	18.20	21.10
HF	44.00	85.60

Conclusion

Failure to achieve a marketable ilmenite concentrate from the Egyptian beach black sand deposit by physical technique with high yield renders proper hydrometallurgical treatment quite necessary. More than 85% of titanium (with 44% of the total iron) could be dissolved from the Egyptian ilmenite concentrate by applying 6M hydrofluoric acid for about one hour at the boiling temperature with a solid: liquid ratio of 1/4. Compared to the conventional sulfate process, the present treatment process greatly advantageous and economic.

It would be preferable to use a relatively low HF concentration in a manner to decrease iron solubility and to decrease acid loss by evaporation. The latter could indeed be reduced by using a proper reflux condenser

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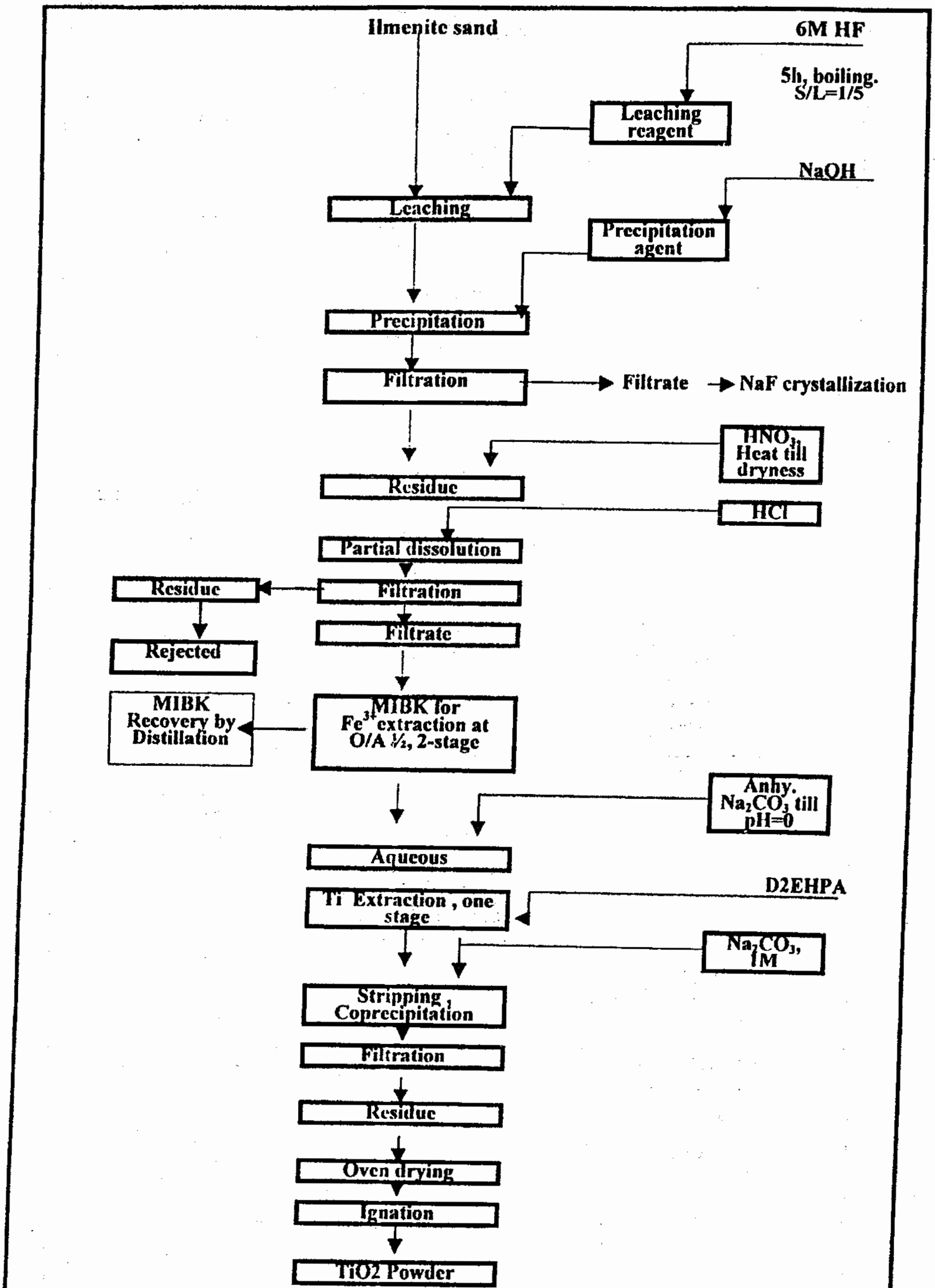

Fig.(1) Flowsheet for preparation of pigment grade titanium dioxide (Biswas et al., 1992)

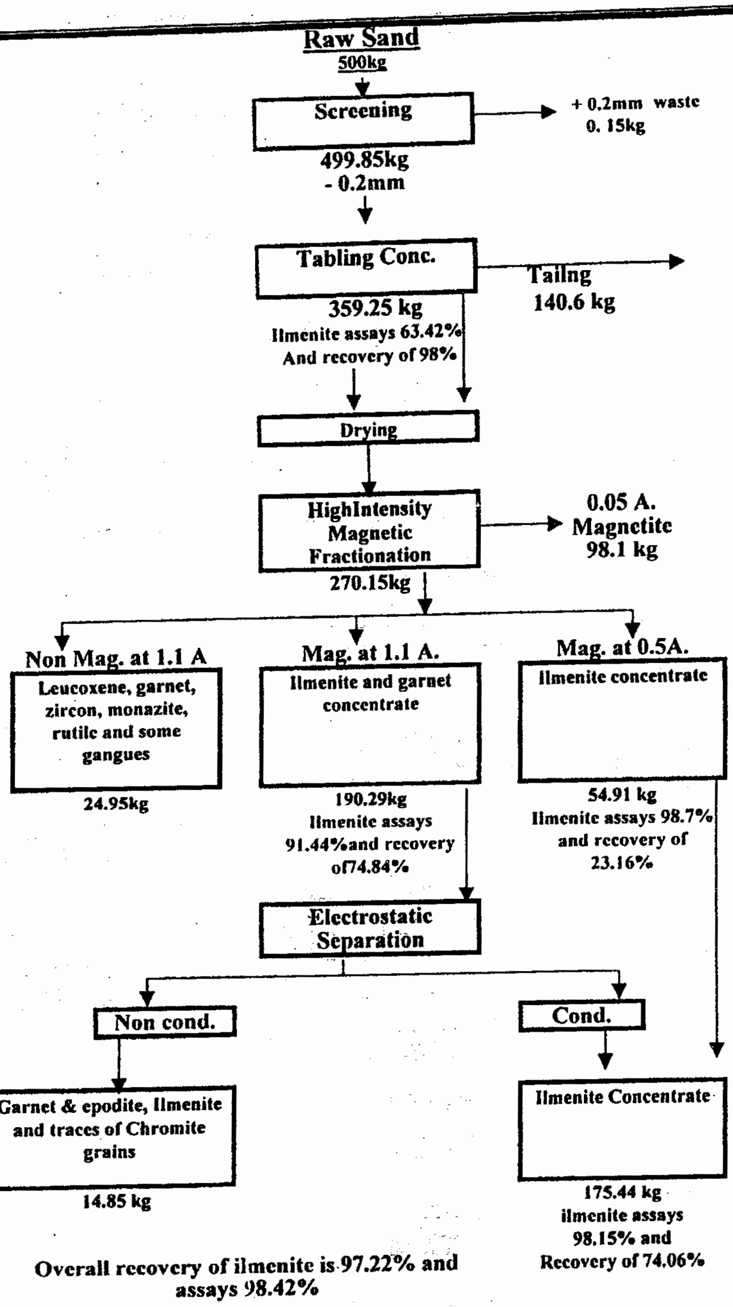

Fig. (2) Flowsheet for up grading Ilmenite from raw sand

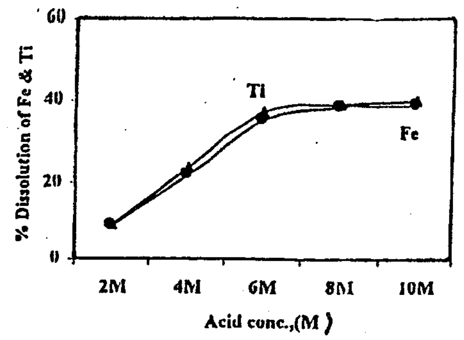

Fig.3.Effect of Acid Conc.,(M) on Fe& Ti Dissolution %

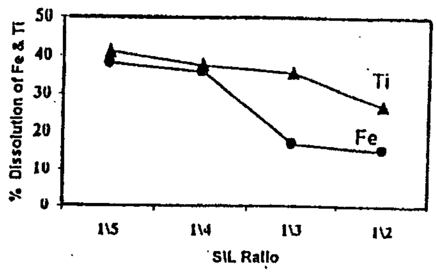

Fig.4 Effect of Solid\Liquid Ratio on Fe & Ti Dissolution %

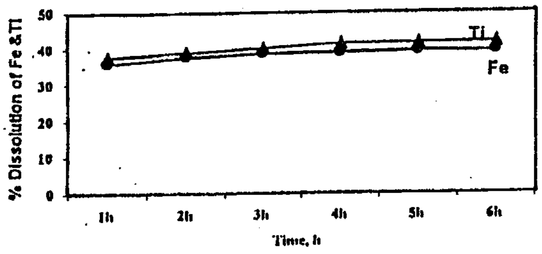

Fig. 5 Effect of Agitation Time on Fe & Ti Dissolution %

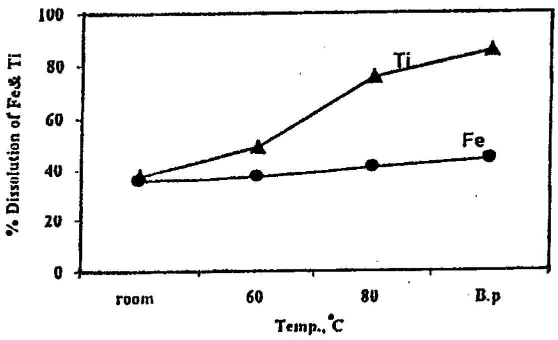

Fig.6. Effect of Temp., on Fe and Ti Dissolution %