

A STRUCTURAL MODEL FOR THE RUSTING OF REDUCED ILMENITE

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ŠTRUKTÚRNY MODEL ODŽELEZENIA REDUKOVANÉHO ILMENITU

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Abstrakt

V novom komerčnom procese výroby syntetického rutilu je kovové železo prítomné v redukovanom ilmenite oxidované na pevný oxid železa použitím chloridu amónneho. Pretože oxidačný proces je veľmi pomalý v prítomnosti chloridu amónneho je potrebné ho urýchliť. Preto sa realizovali experimenty na overenie vplyvu organických zlúčenín. Bolo pozorované, že niektoré organické zlúčeniny ako metanol a acetón v kombinácii s kyselinou mravčou keď sa použijú v prítomnosti chloridu amónneho mali veľmi pozitívny vplyv na priebeh chemickej reakcie. Boli preštudované vplyvy rôznych experimentálnych parametrov, ktoré ovplyvňujú reakciu oxidácie. Študovala sa i kinetika reakcie a bolo realizované modelovanie jej priebehu. Zistilo sa, že reakcia bola kontrolovaná aj rýchlosťou chemickej reakcie aj difúznymi procesmi.

Abstract

In the new commercially followed process for the production of synthetic rutile, metallic iron present in the reduced ilmenite is oxidized to solid iron oxide using NH_4Cl as catalyst. There is necessity for improving the oxidation process, which is very slow in presence of NH_4Cl . Attempts were hence made to study the effects of various organic compounds with a view to accelerate the reaction. It was observed that certain organic compounds like methanol and acetone in combination with formic acid when used along with NH_4Cl had very positive influence on the reaction. The influence of various experimental parameters on the oxidation reaction was investigated. Kinetics of the reaction was studied and the modelling of the reaction was carried out. It was observed that the reaction was chemically as well as diffusion controlled.

Key words: synthetic rutile, ilmenite, rusting, modeling catalytic oxidation

Introduction

Ilmenite (FeTiO_3), which is an ore of titanium, is present abundantly along the coasts of Kerala, Tamil Nadu, Andhra Pradesh and Orissa. Due to the scarcity of natural rutile and cost, beneficiated ilmenite has gained importance as a raw material for the production of titanium metal and pigment through chloride route. Lot of investigations were carried out for beneficiating ilmenite. But many of them suffer from pollution problems as all the iron is leached out with acid. A new process developed by RRL [1] is highly environment friendly which has the following steps. Reduction, rusting, rutilation and acid wash. In this process ilmenite is subjected to carbothermic reduction followed by rusting in presence of a catalyst. In

the rusting step the reduced ilmenite is subjected to oxidation by suspending it in NH_4Cl solution followed by aeration when the iron oxide comes out, which can be separated. The major disadvantage of the above process is that the rusting is most time consuming step, which takes about 16 hrs for completion. Detailed investigations were carried out to accelerate the above reaction with a view to reduce the reaction time. This paper highlights the results of investigations carried out using mixtures of $\text{CH}_3\text{COCH}_3 + \text{HCOOH}$ and $\text{CH}_3\text{OH} + \text{HCOOH}$ along with NH_4Cl [2-4].

Experimental Procedure

Reduced Quilon ilmenite having 76% metallisation was used for the experiments. Laboratory grade and A.R. grade chemicals were used for experiments and chemical analysis respectively.

125 gm of reduced ilmenite was suspended in 500 ml of aqueous solution of 1.5% NH_4Cl catalyst. Air at the rate of 4-5 lit/min was bubbled through the solution, while it was kept stirred at 800 rpm using a mechanical stirrer. 2% acetone or methanol and 1% formic acid were added.

Ilmenite samples were withdrawn at regular intervals of time and the reaction was allowed to run for 4 hrs.

Chemical analysis of the compounds were carried out using standard procedures [5].

XRD studies were done using a Philip's X – ray diffractometer while JSM 5600 scanning electron microscope was used for SEM studies.

Results and Discussion

The chemical reactions taking place during the rusting reaction are

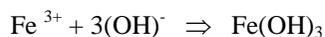
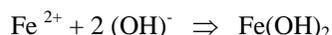
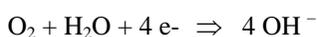


Fig 1 gives the plot of time vs. % iron removal using NH_4Cl , $\text{NH}_4\text{Cl} + \text{acetone} + \text{formic acid}$ and $\text{NH}_4\text{Cl} + \text{methanol} + \text{formic acid}$.

When NH_4Cl alone was used as the catalyst an iron removal of 51% was observed in 4 hrs and then the reaction passivated. When $\text{CH}_3\text{COCH}_3 + \text{HCOOH}$ or $\text{CH}_3\text{OH} + \text{HCOOH}$ were added along with NH_4Cl during rusting the reaction was very fast and the reaction was more less complete within 3 hrs. 86% removal of iron was observed when $\text{CH}_3\text{OH} + \text{HCOOH}$ was added along with NH_4Cl . 90% iron was removed in 3 hrs when $\text{CH}_3\text{COCH}_3 + \text{HCOOH}$ was added along with NH_4Cl .

The major phases present in the reduced ilmenite are anatase, pseudo brookite and metallic iron. In the rusted ilmenite using the above carboxyl compounds along with NH_4Cl the

major phase is anatase. The metallic iron peak has become insignificant confirming that it has been converted to iron oxide or hydroxide.

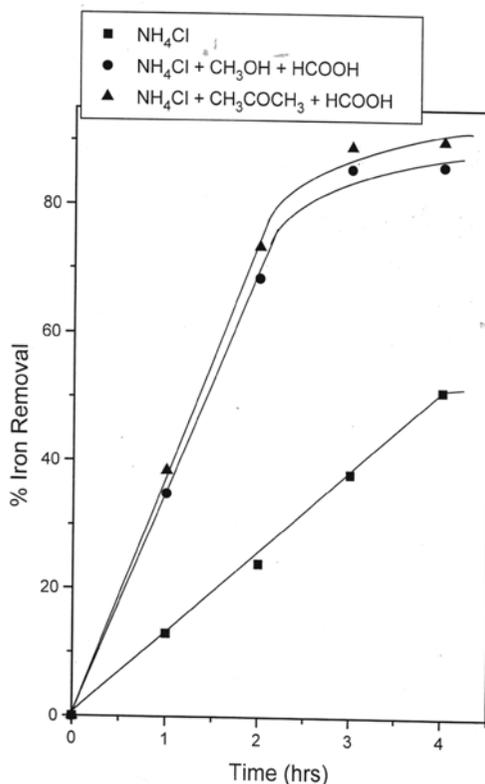


Fig.1 Plot of time vs % iron removal

The SEM pictures of the rusted ilmenite shows a highly porous structures having inter connected plate like formation formed because of the removal of iron entity from the structure. This clearly confirms the removal of iron from the ilmenite particle during rusting. The modelling of the reaction was carried out as follows.



In a porous solid the reaction occurs in a diffuse zone rather than a sharp interface. Let us assume the porous solid to be an aggregate of fine grains having the shape of spheres. There is a gradual change in conversion of solid over the pellet. The external layer will be completely reacted first and the thickness of the completely reacted layer will grow towards the interior of the porous solid.

When pore diffusion is fast compared with the rate of chemical reaction, the concentration of fluid is uniform throughout the pellet and the reaction occurs at a uniform rate. If chemical kinetics is much faster than the rate of diffusion the reaction occurs in a narrow region between the unreacted and the completely reacted zones. We have formulated equations including both chemical kinetics and diffusion and derived the criteria for asymptotic regimes

where a particular step controls the overall rate. The explanations and steps for modeling are as given below are in line with the work reported by Sohn and Szekely [6,7].

Mathematical formulation

Let us consider a porous pellet of volume V_p and of superficial area A , made up of individual particles (grains) having volume and surface area V_g and A_g respectively. The shape of the grains as well as the pellet is considered as spheres.

It is assumed that the solid pellet, which is an agglomeration of spherical grains, reacts with air and catalysts irreversibly.



The additional assumptions are also made as

1. The pseudo-steady state approximation is valid for determining the concentration profile of the fluid reactant within the pellet [8,9].
2. The resistance due to external mass transfer is negligible.
3. Intrapellet diffusion is either equimolar counter diffusion or occurs at low concentrations of diffusing species.
4. Diffusivities are constant throughout the pellet.
5. Diffusion throughout the product layer around the individual grains is not rate limiting.
6. The solid structure is macroscopically uniform and is unaffected by the reaction.

The assumptions are discussed as follows.

Assumption (1) is acceptable for gas solid system [10,11]. Ishida and Wen [12] have shown the external mass transfer is negligible if the pellet Sherwood number, kmR_0/D_e is greater than 100. The assumptions (3,4 and 6) are thought to be the problems of practical interest. It is safe to neglect the effect of diffusion through the product layer, because of small size of grains.

The conservation of fluid reaction is represented as

$$D_e \nabla^2 C_A - \nu_A = 0 \quad (1)$$

Where D_e is the effective diffusion co-efficient within the porous medium, C_A is the reactant concentration and ν_A is the local rate of consumption of A.

Within each grain, the conservation of solid reactant may be described as

$$\rho_B (-\partial r_c / \partial t) = bkC_A \quad (2)$$

Where, ρ_B is the density of reduced ilmenite, r is the distance co-ordinate perpendicular to the moving reaction front, b is the stoichiometric factor and k is the reaction rate constant.

An expression for ν_A may be obtained by determining the surface area for reaction available per unit volume of the pellet.

$$\nu_A = \alpha_\beta k (A_g / V_g) (A_g r_c / F_g V_g)^{F_g - 1} C_A \quad (3)$$

Where, α_β is the volume fraction of the pellet occupied by solid B, A_g is the external surface of an individual grain, V_g is the volume of the grain, F_g is the shape factor. Shape factor for sphere is 3.

'Equation (1) and (2)' can be expressed in dimensionless form for introducing dimensionless variables [13].

$$\Psi \equiv C_A / C_{AB} \quad (4)$$

$$\xi \equiv A_g r_c / F_g V_g = r_c / r_g \quad (5)$$

$$t^* \equiv (bkC_{AB} A_g / \rho_B F_g V_g) t \quad (6)$$

$$\eta \equiv A_p R / F_p V_p = R / R_p \quad (7)$$

$$\sigma \equiv F_p V_p / A_p (\alpha_\beta k A_g / D_e V_g)^{1/2} \quad (8)$$

t is the total time of reaction, F_p Shape factor of the pellet ie, 3. A_p external surface area of the pellet ($4\pi R^2 = 1$ already assumed), V_p Volume of the pellet, R is the distance from the centre of symmetry in the pellet.

The dimensionless form of equation (1) and (2) is

$$\nabla^{*2} \Psi - \sigma^2 \Psi \xi^{F_g-1} = 0 \quad (9)$$

$$\partial \xi / \partial t^* = -\Psi \quad (10)$$

Where, ∇^* is the Laplacian operator with η as the position co-ordinate.

The initial boundary conditions for 'equations (9) and (10)' are

$$\xi = 1 \quad \text{at } t^* = 0 \quad (11)$$

$$\Psi = 1 \quad \text{at } \eta = 1 \quad (12)$$

$$\partial \Psi / \partial \eta = 0 \quad \text{at } \eta = 0 \quad (13)$$

η is the length co-ordinate in ∇ operator (13).

In terms of the parameters used in the formulation the overall extent of the reaction is defined as

$$X = \int \eta^{F_p-1} (1 - \xi^{F_g}) \partial \eta / \int \eta^{F_p-1} \partial \eta \quad (14)$$

The dimensionless representation governing equation shows the dependent variables ξ and Ψ are related to t^* and η and the single parameter which appears in the formulation as σ .

The quantity of σ incorporates both structural and kinetic parameters.

Asymptotic Behaviour

When σ approaches zero, the overall rate is controlled by chemical kinetics, and diffusion within the pellet is rapid compared with the rate of the chemical reaction. Further ξ is independent of η , although still a function t^* . Under these conditions equation (10) is readily integrated to obtain

$$\xi = 1 - t^* \quad \text{for } 0 \leq t^* \leq 1$$

$$\text{and } \xi = 0 \quad \text{for } t^* \geq 1 \quad (15)$$

Using equation (14) we get relationship between X and t^*

$$t^* = 1 - (1-X)^{1/F_g} \equiv g_{F_g}(X) \quad (16)$$

$g_{F_g}(X)$ refers to the value of t^* within asymptotic regime where $\sigma \rightarrow 0$. From experimental data it is understood diffusion within the pellet was not rate controlling.

(ii) When σ approaches infinity

The overall rate is controlled by the diffusion of the gaseous reactant within the pellet. This corresponds to the shrinking core model.

$$P_{F_p}(X) = 2 F_p b D_e C_{AB} / \alpha_\beta \rho_B (A_p / F_p V_p)^2 t \quad (17)$$

$$2 F_g F_p / \sigma^2 t^* = t^* / \sigma^{\wedge 2} \quad (18)$$

Where $\sigma^{\wedge 2} = \sigma^2 / 2 F_g F_p$

Equation (17) provides a convenient means of determining the effective diffusivity by plotting experimental data obtained under diffusion control.

$$\sigma^{\wedge} = \sigma / (2 F_g F_p)^{1/2} = V_p / A_p [\alpha_\beta k F_p / 2 D_e (A_g / F_g V_g)]^{1/2} \quad (19)$$

Analytical Solutions

Equation (16) and (18) correspond to asymptotic solutions for pure chemical control and pure diffusion control respectively.

Since the grains are spherical $F_g = 3$ equation (9) becomes

$$(\partial^2 / \partial \eta^2 - \sigma \xi^2) \Psi = 0 \quad (9a)$$

$$\Psi = \cos h(\sigma \xi \eta) / \cos h(\sigma \xi) \quad (20)$$

$$\partial \xi / \partial t^* = -\Psi \quad (10)$$

$$= t^* [1 - \cos h(\sigma \xi \eta) / \cos h(\sigma \xi)] \quad (21)$$

The time required to achieve the complete reaction of the pellet is

$$t^*_{x=1} = 1 + \sigma^{\wedge 2} \quad (22)$$

The rate of reaction is independent of the solid reaction concentration.

The reaction of a porous solid with a fluid involves chemical reaction and intrapellet diffusion occurring in parallel. The grain model is the recent development in this area. The models have been tested against experiments and found to describe the reaction of porous solids reasonably well.

The experimental values were tested with the equations obtained through the development of structural model and was verified by plotting in the graphs. Fig.2, 3 and 4 show that, the structural model goes in hand with the experimental value.

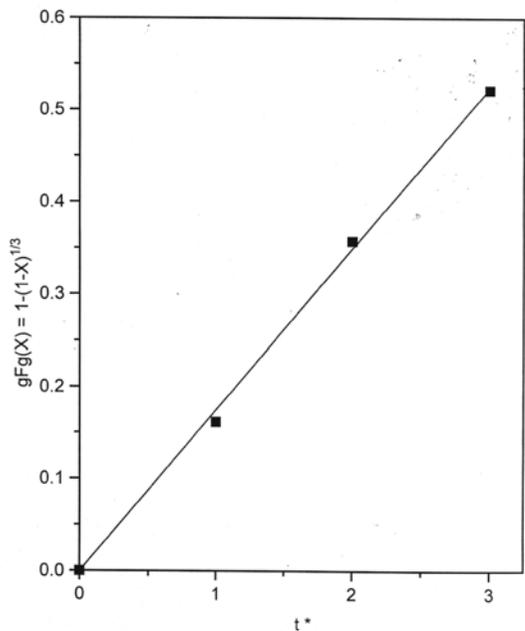


Fig.2 Conversion function vs. Reduced time for small of σ

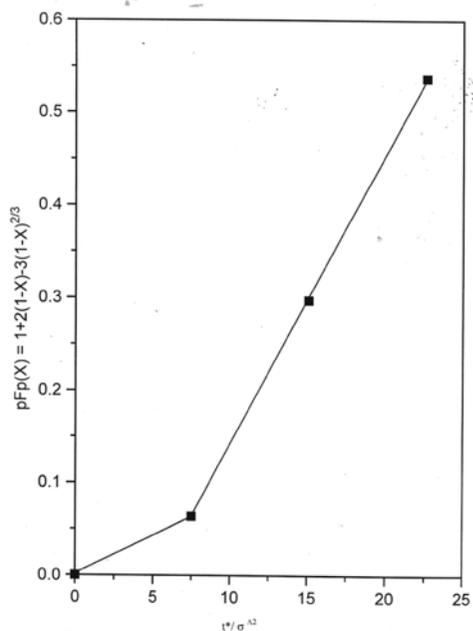


Fig.3 Conversion function vs. reduced time for large values of σ

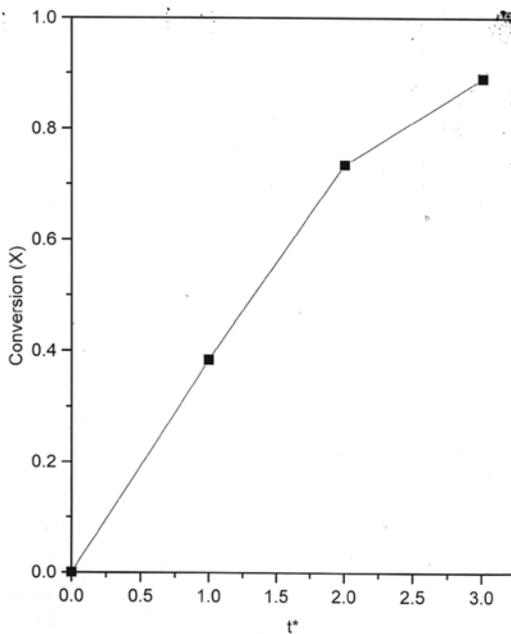


Fig.4 Comparison of approximate solution with exact solution

The straight line obtained by plotting t^* vs. $gF_g(X) = 1-(1-X)^{1/3}$ proves that the reaction is controlled by surface chemical or topochemical.

The graph obtained by plotting t^*/σ^2 vs. $pF_p(X) = 1+2(1-X)-3(1-X)^2/3$ is an evidence of the diffusion controlled reaction. There is good agreement between the model developed and the experimental data, which shows that the model developed is correct and suitable.

The graph obtained by plotting t^* vs. conversion (X) is also similar to the one which we expect from the theoretical data.

Conclusion

The following conclusions can be drawn from the results of the above investigations.

1. The mixtures of methanol and formic acid along with NH_4Cl are more efficient for the iron removal from reduced ilmenite
2. Acetone formic acid mixture is better than methanol and formic acid as a catalyst.
3. About 90% of iron removal could be achieved using acetone and formic acid in place of 51% for NH_4Cl alone.
4. The product obtained after rusting had a TiO_2 content of 95.85% after rusting for 3 hrs.
5. XRD and SEM studies show the structural and morphological changes taking place during rusting.
6. Modeling studies confirm that the reaction is diffusion as well as chemically controlled.

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