Kinetic Studies on the Chlorination of Zircon

A. C. Bidaye, S. Venkatachalam* and C. K. Gupta[1]

Materials Group, Bhabha Atomic Research Centre, Mumbai, India.
**Indian Institute of Technology, Mumbai, India.*

(Received January 4, 2002; final form March 15, 2002)

ABSTRACT

This paper reports on an investigation on the zircon chlorination process. The chlorination was conducted (i) with static zircon-coke powder mixtures in horizontal and vertical reactors, (ii) with zircon-coke mixed powder compacts in the two reactors, and (iii) with a sintered zircon disc and a grooved carbon disc. Experiments with the zircon and carbon discs clearly revealed that physical contact between zircon and coke was mandatory for the chlorination to occur. It was also observed that a faster chlorination rate and a higher extent of chlorination with static charge were achieved if the charge was compacted prior to chlorination. This was explained as being due to the formation of fine zircon and coke particles in intimate contact with each other. Due to the complexity of zircon carbo-chlorination, system specific rate expressions have been proposed. For a loose charge in a horizontal static bed reactor, the rate expression was linear, while for a compacted (and crumbled) zircon-coke mixture held in a vertical pipe reactor the reduced time plots technique was used to arrive at the rate expression, which turned out to be the Ginstling-Brounshtein expression.

I. INTRODUCTION

A survey of the literature on zircon chlorination revealed that there is no unanimity either on the values of the kinetic parameters or on the form of the rate expression or on the reaction mechanism followed by the chlorination. Hence this investigation was conducted to gain some insight into the chlorination process. In an earlier paper /1/ the effect of various process parameters on the rate and extent of zircon chlorination was reported. It was observed that the extent of reaction i.e. the fraction of zircon reacted, α, in the static bed reactor was limited to 0.35. It was noticed that the reaction, when it stopped, was far removed from equilibrium; just the reaction rate had become immeasurably small. Existing literature on zircon chlorination /2,3,4/ was unable to provide an explanation for this observation. And, in general, despite commercial operation of zircon chlorinators, the kinetics of zircon carbo-chlorination is not well understood and different investigators have reported not only different values for the kinetic parameters (activation energy, E_a and pre-exponential constant, A), but also different forms of the kinetic expression (Table 1). Hence attempts were made to understand the kinetics of zircon carbo-chlorination, to find an explanation for the cessation of the chlorination, to achieve higher levels of conversion and to propose a kinetic law.

II. THEORETICAL

The progress of a reaction is frequently charted in terms of the fractional conversion of the reactant charged only initially. The general form of the rate expression is

---

[1] To whom correspondence should be addressed

Table 1

Results of zircon carbo-chlorination investigations.

Investigators	System	Rate expression	Activation energy, kJ/mole
Spink *et al.* /2/	Horizontal Static Bed Reactor	$r=3.04C^{0\ 32}(Z/4)^{0\ 15}\ e^{-E/RT}$	16.8
Spink *et al.* /3/	Electrothermal Fluidized Bed Reactor	$r=23.625[AV_r(R_{av})^{0\ 23}e^{-1}$ E/RT	44.2
Almond /5/	Fluidized Bed Reactor	Nil	75.2
Sparling *et al.* /4/	Vertical Static Bed Reactor (Carbon deficient system)	Nil	134
	Vertical Static Bed Reactor (Zircon deficient system)	Nil	150
	Fluidized Bed Reactor	Nil	81-157
Stefanyuk *et al.* /6/	Horizontal Static Bed Reactor	$1-(1-\alpha)^{1/3} = (k/r_0)t$	97.6

r = reaction rate; C= av. mole fraction of Cl_2 in the reaction gas; Z = R_{av} = average carbon/zircon molar ratio; E = act. energy; R =gas const.; A = equivalent surface area of zircon particles; V_R = bed volume per initial surface area of particles; α = degree of chlorination; k_r = specific radial reaction rate; t = reaction duration; r_0 = average particle dia.

$$g(\alpha) = kt \qquad (1)$$

where t is the time taken to attain α fraction of the maximum possible conversion and k is the rate constant. It is assumed that the rate expression has two distinct components: k, the rate constant, dependent on the system characteristics, and $g(\alpha)$, determined solely by the reaction mechanism. If different reaction systems have the same reaction mechanism, plots of $g(\alpha)$ versus time will have the same shape, with k acting as a scaling factor. A preliminary identification of this rate controlling mechanism can be made by using the so called reduced time plots first introduced by Sharp *et al.* /7/ and Geiss /8/. In this technique k is eliminated in the following manner.

If t_m is the time required to reach m ($0 < m < 1$) fractional conversion (m is generally chosen to be half the maximum conversion attained during the investigation) then we can write from eqn. (1)

$$g(\alpha_m) = kt_m \qquad (2)$$

Keeping k constant and combining eqns. (1) and (2), we get

$$g(\alpha) = A(t/t_m) \qquad (3)$$

where A is a calculated constant depending on the form of $g(\alpha)$ and the value of m, but independent of k, temperature, and other factors affecting the reaction rate. Eqn. (3), which is dimensionless, is thus exclusively dependent on the reaction mechanism, which can be determined by plotting α vs t/t_m plots and comparing these plots with standard α vs t/t_m plots. The standard plots can be theoretical plots for reaction models assuming a particular rate-controlling step; alternately, they can be experimental plots for reactions with a known rate controlling mechanism. Theoretically derived rate expressions, tabulated values of α vs t/t_m for various rate expressions and graphical plots of several rate expressions in terms of reduced time can be found in the literature /9,10,11/. Some selected expressions have been plotted in Fig. 6.

Despite certain limitations, discussed by Ray /10/, the reduced time plots approach, when used with due caution, is a powerful tool for initial identification of the rate controlling mechanism and establishing the rate expression.

III. EXPERIMENTAL

A Materials

The materials, *viz.* zircon sand from Chavara, Kerela, India, calcined petroleum coke and bottled chlorine, used during the investigation, were the same as described in an earlier paper /1/.

B Equipment

1. *The Static Bed Reactor*

The Static Bed Reactor, consisting of a quartz tube placed inside a tubular furnace, was also the same as that described in reference 1. The charge, either loose or compacted, was placed in a silica boat located at the centre of the furnace.

2. *Muffle Furnace for Chlorination of Zircon-Carbon Tablets.*

A box type muffle furnace, with silicon carbide heating elements, was used for the chlorination of zircon-carbon tablets. The furnace had a rectangular opening on one of its faces for charging and this could be closed with an insulating brick. A hole was drilled in this brick and a one end closed silica tube inserted into the furnace as shown in Fig. 1. The silica tube had provision for evacuation and also for filling with nitrogen/chlorine gas.

3. *Vertical Pipe Reactor*

A sketch of the system is shown in Fig. 2. The reactor was made from a 25 mm dia. transparent silica tube. A 21 mm dia. porous sintered silica disc was fitted at the centre of the vertical section. The powder charge rested on this disc. A thermocouple was tied to the outer side of the tube with its tip at the centre of the charge. Both ends of the silica reactor were water cooled. While the heating furnace, the gas monitoring system and the scrubbing system were the same as for the static bed reactor unit, the gas (CO) issuing from the second scrubbing bottle was collected in an inverted graduated measuring cylinder as shown in the sketch.

C Procedure

1. *The Static Bed Reactor*

The static bed chlorinator was used for chlorination of the uncompacted charge as well as the compacted charge. The chlorination of the uncompacted charge in the static bed reactor has been described in the earlier paper. Chlorination of zircon-coke compacts was carried out as follows. Six identical 10 mm diameter pellets were prepared by mixing 2.14 g (-230+325 mesh) zircon with 1.12 g (-140+200 mesh) coke and compacting at 2.75 x 10^5 kPa. Considerable difficulty was experienced in compacting the charge, and the addition of a few drops of distilled water or acetone to the charge prior to compaction was found to have a beneficial effect. The tablets were of just handling strength and could be easily crumbled with gentle pressure. Three of these pellets were gently crumbled, without any further attrition. Separately, each of the three uncrumbled tablets and the three crumbled charges were held in a silica boat and charged into the furnace for chlorination. The chlorination was conducted for various durations and the weight loss of the solid charge on chlorination was used as a measure of the extent of the reaction.

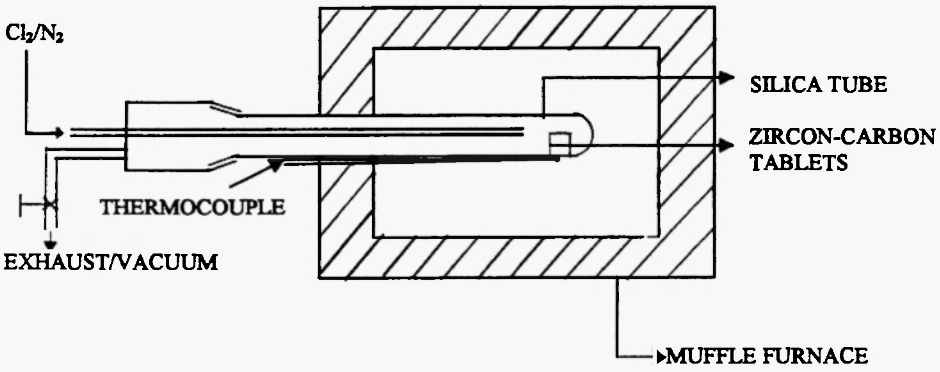

Fig. 1: Set-up for chlorination of zircon carbon tablets.

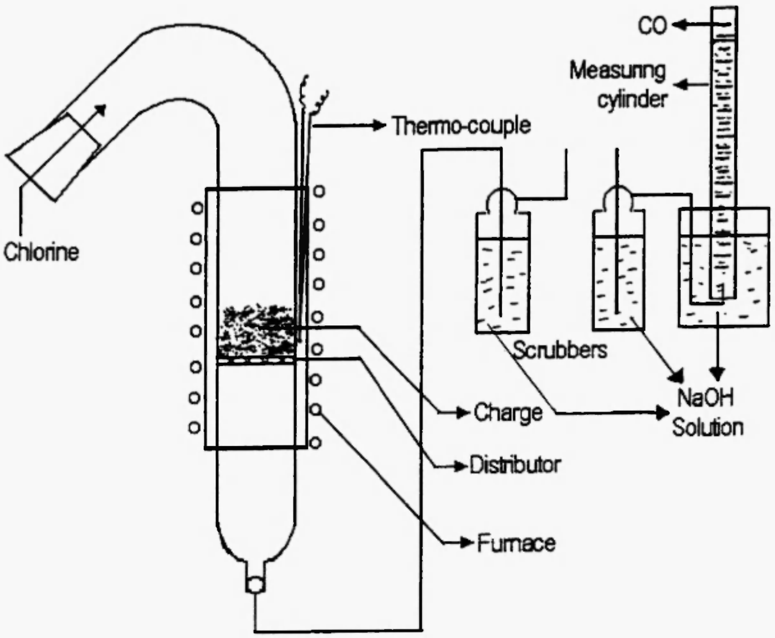

Fig. 2: The Vertical Pipe Reactor.

Since it is extremely difficult to ensure complete condensation and collection of pure chloride, no effort was made to study the progress of the reaction on the basis of the weight of the zirconium chloride formed. Instead, the weight of the sample before and after the reaction was monitored. The chlorides condensed in the cooler regions of the system, which had to be cleaned periodically to prevent the system from getting choked.

The following reaction stoichiometry /1,2,4,5/ was used to calculate the fractional conversion of zircon:

$$ZrSiO_{4(s)} + 4C_{(s)} + 4Cl_{2(g)} \rightarrow ZrCl_{4(g)} + SiCl_{4(g)} + 4CO_{(g)} \quad (4)$$

The fraction of zircon reacted, α_z, was calculated from the recorded weight loss of the sample during chlorination, w_l, as follows.

$$\alpha_z = 0.792 \frac{w_l}{w_z} \quad (5)$$

where w_z is the initial weight of zircon and the coefficient (0.792) arises due to stoichiometric considerations.

2. *Chlorination of zircon-carbon tablets*

Similar to the experiment conducted by Bergholm /12/, chlorination of zircon and graphite tablets was attempted. Two tablets, each of 10 mm dia. and about 7 mm thick, one of sintered zircon and the other cut from a graphite rod, were placed one on top of the other, circular faces in contact. The graphite tablet had a rectangular groove, 0.5 mm deep and 2 mm wide, cut diametrically across the face in contact with the zircon tablet (Fig. 3), so that some part of the tablet was in physical contact with the zircon tablet and some part was not. The tablets were initially heated under IOLAR (high purity) N_2 at 1673 K. Subsequently the tablets were chlorinated at temperatures up to 1673 K. The tablets were individually weighed and their dimensions measured both before and after chlorination.

3. *Vertical Pipe Reactor*

To overcome non-uniform and non-reproducible gas-solid contacting occurring in the static bed reactor, chlorination in a vertical pipe reactor was explored. Based on experimental results discussed later, the following procedure was finally adopted for kinetics studies in the vertical pipe reactor. Cylindrical tablets of 10 mm dia. prepared, at 3×10^5 kPa, from mixtures of weighed amounts of (-400 mesh) zircon and (-400 mesh) coke, were held in the cooler horizontal portion of the reactor while it was being heated under N_2 gas flowing from top to bottom. When the desired temperature was attained, the

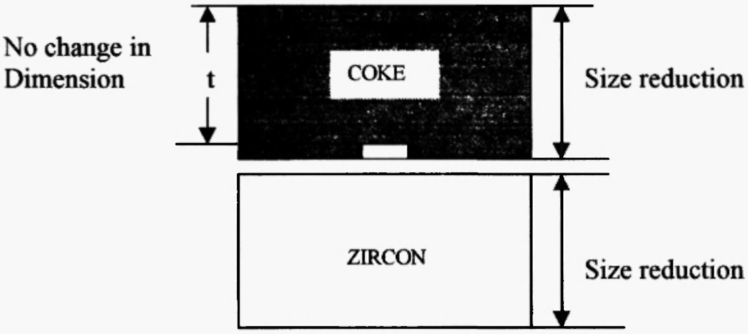

Fig. 3: Grooved Pellet Experiment.

N_2 gas flow was discontinued, the reactor was flushed with Cl_2 gas, and then the tablets were quickly pushed down the reactor and onto the gas distribution disc, where they immediately crumbled to powder. The heating continued under Cl_2 gas flowing from top to bottom. The reaction began almost instantly with the formation of chloride fumes in the cooler regions of the reactor. The chlorides and the unreacted chlorine were thoroughly scrubbed in the caustic soda solution while CO was allowed to collect in the inverted measuring cylinder. By monitoring the volume of CO collected as a function of time, the fractional conversion, say of zircon, α_z, could be calculated. Corrections due to the increase in the temperature (and thereby in the volume) of the scrubbing solution and of the water vapour carryover into the measuring cylinder were duly incorporated after conducting blank trial runs. The results were counterchecked by weighing the residual powder after chlorination.

IV. RESULTS AND DISCUSSION

1. Static Bed Reactor :

In an earlier paper /1/ it was discussed that samples of uncompacted zircon-coke mixtures initially reacted with Cl_2 at a constant rate followed by a plateau region where the reaction had virtually stalled, as shown in Fig. 4. The following possibilities were considered for this cessation of the reaction in the presence of all the three reactants:

i) The formation of an impervious and inert film on one of the solid reactants.

ii) The possibility that once the solid reactants at the surface were consumed, a layer of only one solid reactant, say coke (100% excess over the stoichiometric requirement of coke was present in the initial charge), was left at the surface. This would require the chlorine to penetrate past this layer, and also the chloride (and CO) product gases to cross this layer in escaping from the interior, and this would substantially reduce the reaction rate.

However, as discussed in reference 1, these two possibilities were ruled out. Another possibility considered was that of the necessity of coke-zircon contact points for the reaction to progress. But it was felt that the results of the chlorination experiments conducted in the static bed reactor with uncompacted charge were not conclusive and further experiments were needed to justify such a conclusion.

Accordingly, chlorination experiments were conducted after compacting the solid zircon-coke charge to achieve better zircon-coke contacts. The results of these experiments are given in Table 2, and can be summarized as follows.

i) On compaction, the original zircon and coke particles were crushed to a very fine size; zircon to ≈ 1µm and coke to < 1 µm. However, during gentle hand crumbling of the 10 mm dia. tablets to 2-3 mm sized pieces, no additional size reduction of the zircon or coke particles occurred.

ii) The extent of chlorination was greater after compaction as compared to the uncompacted charge.

iii) The rate of reaction was faster for the compacted and crumbled charge than for the merely compacted charge.

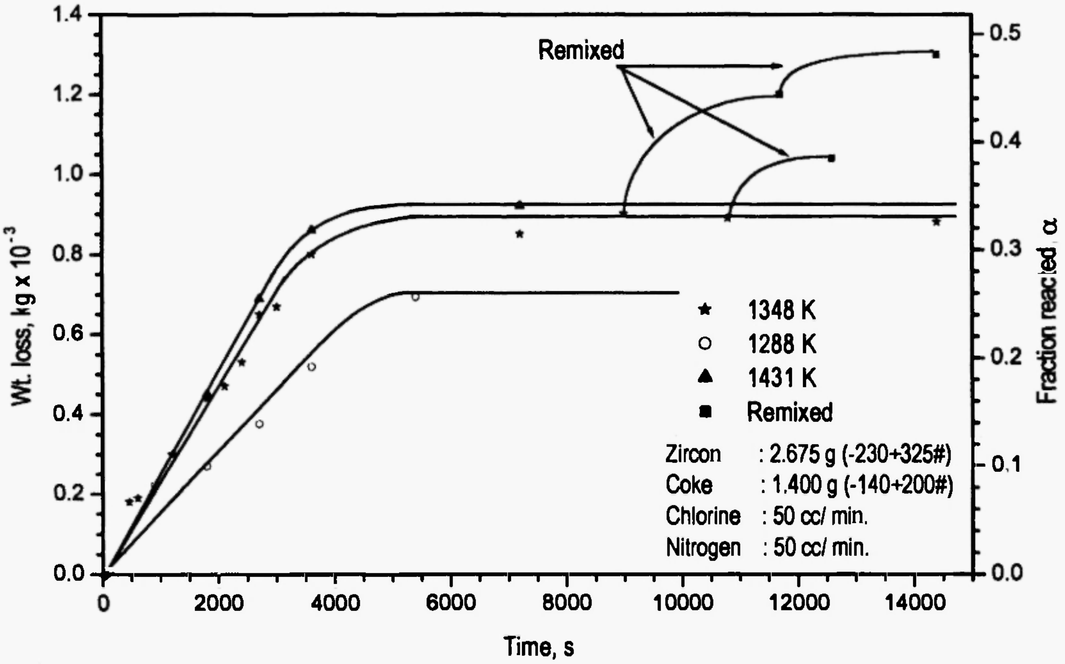

Fig. 4: Effect of reaction duration on weight loss in a Horizontal Static Bed Reactor.

Table 2

Effect of pelletising (and recrumbling) of charge on fraction reacted in a Static Bed Reactor

Zircon : -230+325 mesh
Coke : -140+200 mesh
Temperature : 1248 K
N_2 flow : 0.83 cm^3/sec.
Cl_2 flow : 0.83 cm^3/sec.
Pelletising pressure : 2.75 × 10^5 kPa

Sr. No.	Time (mins)	Fraction Reacted	
		Only pelletised	Pelletised/ Recrumbled
1	30	0.38	0.50
2	45	0.48	0.55
3	60	0.56	0.58

iv) During the reaction the compacts crumbled to powder. The crumbling started at the top and progressed downwards. For very short duration experiments, the lower portions of the cylindrical compacts resting on the boat had retained their shapes even as the top portions had crumbled. This suggested that the reaction started at the top and the pellets probably crumbled because the chlorine attacked the contact points.

The larger extent of conversion as also the higher rate of chlorination brought about by compaction could be due to the larger total particle surface area resulting from the comminution effect of compaction as also due to the larger number of and more intimate zircon-coke contacts resulting from the compaction. Thus, this set of experiments gave another strong indication that zircon-coke contacts were essential for the chlorination.

2. Chlorination of a zircon tablet and a grooved carbon tablet

When the zircon–coke tablets were chlorinated, no reaction was detected up to a temperature of 1573 K even after a period of 5 hours. At 1673 K approximately 5 % reduction in weight of the zircon tablet and a 3 % reduction in weight of the coke tablet was noticed after 5 hours of chlorination with pure Cl_2. [The initial weights of the zircon and coke tablets were neither equal nor in stoichiometric proportion. However, the final weight loss was in stoichiometric proportion as per Eq. 4.] There was no change in the diameter of the tablets. The thickness of the zircon and coke tablets had, however, decreased by a matching 5 % and 3 % respectively. But there was no change in the dimension of the coke tablet below the groove as shown in Fig. 3 (dimension t). If the chlorination reaction involved formation and gas phase transport of gaseous intermediates, the groove should have been attacked, but if physical contact was essential, no reaction could occur in the groove. This experiment clearly demonstrated that physical contact between zircon and coke is of paramount importance in zircon carbochlorination. The limited extent of reaction at the contact interface can be explained as being due to the difficulty of chlorine penetrating between the two tablets as also of the reaction products coming out.

The contact model can be used to explain the cessation of reaction in the static bed reactor as follows. When the zircon-coke mixture is initially charged, zircon-coke contact points exist and the reaction commences at these points. As these points are consumed, the residual charge settles onto itself, re-establishing zircon-coke contact. However, after some time, due to arch formation amongst the particles, the charge will be unable to settle down and this, coupled with the initial zircon-coke segregation due to imperfect mixing, would result in no reaction in spite of the presence of a large excess of the reactants. This explains why when the charge is remixed, the reaction commences immediately.

The formation of an intermediate carbide phase was also considered. The carbide phase can form by the following reaction

$$ZrSiO_4 + 6C \rightarrow ZrC + SiC + 4CO \qquad (6)$$

Such a reaction would have resulted in weight loss of the charge due to the formation of volatile CO. However, no change in weight was detected when powdered zircon and carbon samples were heated in an inert atmosphere at 1423 K for over 4 hrs. Additionally, the XRD pattern of the zircon tablet and the zircon-coke mixture after reaction did not reveal the presence of any additional phase.

3. Vertical Pipe Reactor

To overcome non-uniform and non-reproducible gas-solid contacting, chlorination in a vertical pipe reactor was explored. When the charge was placed on top of the porous silica plate distributor and gas passed from the bottom, then, at low flow rates, due to the inherent non-homogeneity of pore size in such sintered discs, channeling occurred so that gas could be seen bubbling at a few spots only. Changing the disc did not solve the problem. At high flow rates, the gas distribution appeared to be uniform, but the entire bed was in a fluidized state. Since kinetics of a fluidized bed is a field in itself and chlorination of zircon in a fluidized bed reactor has been reported elsewhere /13/, an alternate technique was adopted. Since gas distribution appeared to be uniform at high flow rates (all the pores becoming active) it was decided to pass gas at high flow rates in the reverse direction, i.e. from top to bottom, so that fresh gas for the reaction would be uniformly available at all sites.

Since higher conversion in the boat experiments could be attained only after mixing and compaction, the charge for the vertical pipe reactor runs was also compacted at around 3 x 10^5 kPa. The charge composition was kept stoichiometric to prevent excess unreacted solids from forming a barrier to gas penetration.

It was also decided to use pure chlorine for this set of experiments. As described in Section III.C.3, the exhaust gas was passed through a set of scrubbers so that only pure CO escaped and was collected in an inverted measuring cylinder. By monitoring these volume readings, a complete and continuous record of the chlorination was created. At the end of the chlorination run, the unreacted charge was weighed and the weight loss checked against the volume of CO collected. After the indicated corrections, the agreement was generally found to be within ±3%.

Three experiments were conducted in this fashion. The results are presented in Fig. 5. In the first two cases, the temperature was 1288 K and 1373 K respectively, while in the third case, the unreacted charge of the run at 1373 K was remixed and recompacted at the same pressure and rechlorinated again at 1373 K. When the charge, which had stopped reacting, was thus recharged, the reaction commenced immediately with the evolution of copious chloride fumes. However, the reaction rapidly slowed down and practically stopped in 10 minutes, by which time about 20 % of the recharged material had reacted.

Reduced time plots for the reaction of the fresh charge are shown in Fig. 6. Plots for some standard reaction

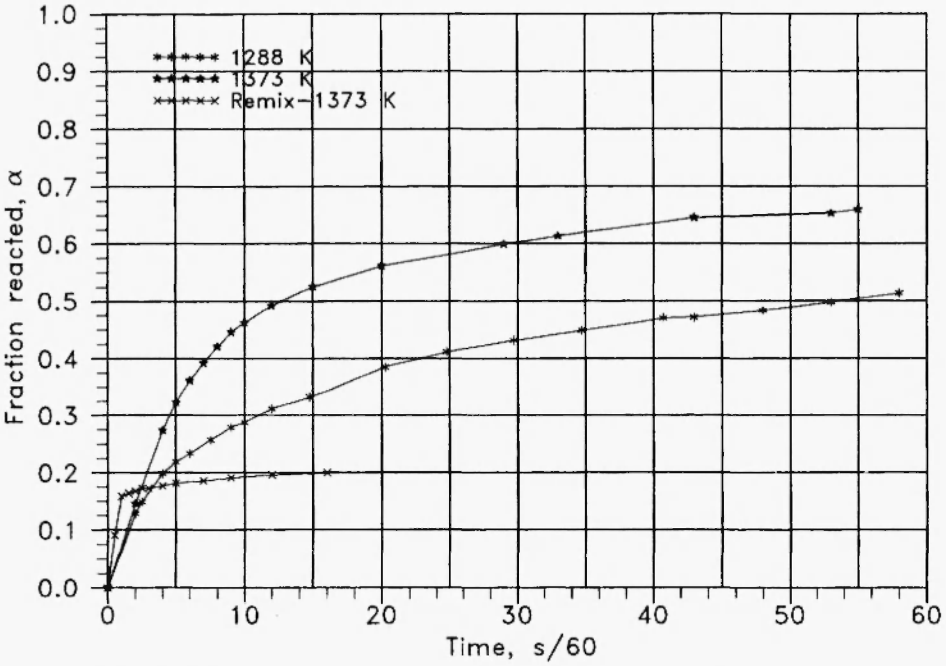

Fig. 5: Fractional conversion vs time in a Vertical Pipe Reactor.

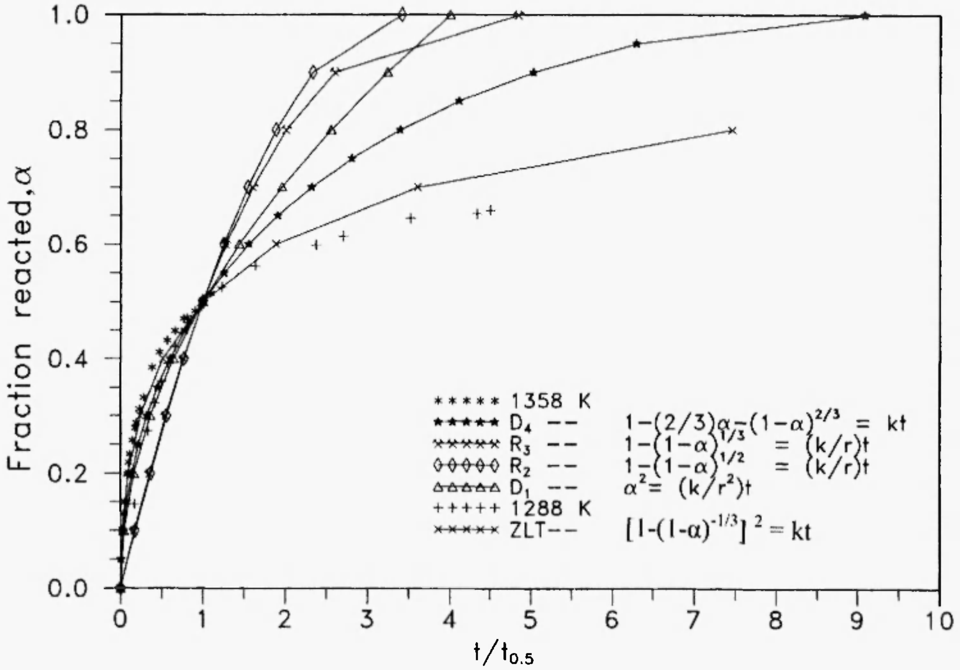

Fig. 6: Experimental data points and standard reduced time plots in a Vertical Static Bed Reactor.

models have also been superimposed. As can be seen, the data does not fit any of the standard models.

As in the horizontal boat assembly, 100% conversion of zircon was not possible even in the vertical pipe reactor. However, it had been noted even in the horizontal boat experiments that total conversion under identical conditions was not reproducible and varied apparently due to variations in mixing. Thus the final conversions reached in the vertical pipe experiments at 1288 K and 1373 K were considered to be the maximum possible conversions under those particular conditions of mixing. Using these values of α_{max} for division of the α's calculated on the basis of the theoretically possible maximum conversion, a new set of fractional conversion values, α', were obtained. When these sets of values were superimposed on the standard reduced time plots, an excellent fit was found with the Ginstling-Brounshtein (GB) curve (Fig. 7). The GB expression thus appears to be a rate expression, which is able to correlate the measured data for the chlorination of zircon in a vertical pipe reactor.

However, it may be noted that despite the excellent fit, the GB model is physically inconsistent with the formulation on which this rate model is based. The GB model has been developed for a reaction wherein the particles are of uniform size, and this size remains constant throughout the course of the reaction despite the formation of a product layer, and the reaction rate is controlled by diffusion of the gaseous reactant across the solid product layer to the unreacted core. The zircon (and coke) particles shrink in size during reaction and leave behind no apparent product layer

4. Proposed rate expression

It is difficult to quantify precisely the zircon carbochlorination system (in terms of zircon-coke contacts, exact chlorine concentration at reaction sites, etc.) nor does there exist a well accepted, clearly defined reaction mechanism for the chlorination. As such, a purely mechanistic approach cannot be used to derive the rate expression for this reaction. And since existing rate expressions (Table 1) were found to be inapplicable to the data generated in the present investigation, the following empirical relations are being proposed.

I. For zircon-coke charge in a horizontal boat

$\alpha = kt$

The activation energy value was 200 kJ/mol below 1273 K while above this temperature and up to the temperature investigated (1431 K) it was found to be 34 kJ/mol.

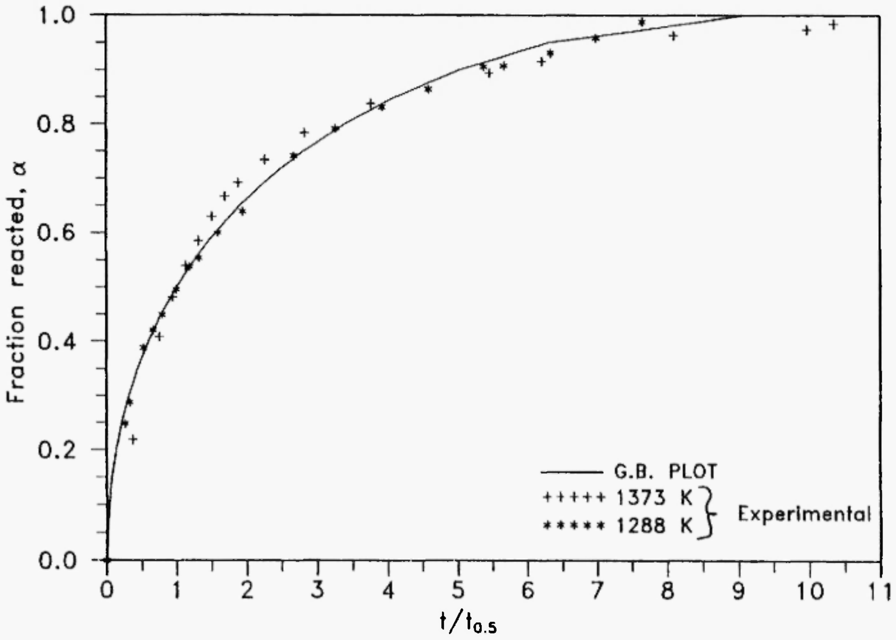

Fig. 7: Experimental data points (modified) and the Ginstling-Brounshtein plot.

II. For static zircon-coke charge in a vertical reactor

$1 - (2/3)\alpha - (1-\alpha)^{2/3} = kt.$

The activation energy value for this system (in the temperature range 1278 to 1431 K) was found to be around 60 kJ/mol while the pre-exponential constant under the given conditions was found to be 1.7 x 10^{-2}/sec..

V CONCLUSION

Zircon carbo-chlorination is a complex process and the rate of reaction depends on the values of a large number of process parameters. It is due to this complexity that different investigators have reported different values for the kinetic parameters like activation energy, order of reaction etc. as also different forms of the rate expression. However, the present investigation has clearly established that zircon-coke physical contact is a pre-requisite for the reaction to occur. For higher rates of chlorination as also for larger extent of reaction, closely compacted fine zircon-coke powder is beneficial. A single rate expression fitting data from different chlorination systems could not be found and separate system specific expressions have been proposed.

REFERENCES

1. A.C. Bidaye, S. Venkatachalam and C.K. Gupta, *Metall. Trans. B*, **30B**, 205-213 (1999).
2. A.A. Manieh and D.R. Spink, *Can. Met. Quar.*, **12**, (3), 331-340 (1973).
3. A.A. Maneih, D. Scott and D.R. Spink, *Can. J. Chem. Engg*, **52**, 507- 514 (1974).
4. D.W. Sparling and J.R. Glastonbury, *Australian J.M.M. Conf.*, Western Australia, 455-463, 1973.
5. J.C. Almond Ph. D. Thesis, Univ. of Washington, Seattle, 1966.
6. S.L. Stefanyuk and I.S. Morozov, *Zhur. Prikl. Khim.*, **38** (4), 729, (1965), cited in *C.A.* **63**:3665d.
7. J.H. Sharp, G.W. Brindley and B.N. Narhari Achar, *J. Amer. Ceram. Soc.*, **49**, 379-82, (1966).
8. E.A. Geiss, *J. Amer. Ceram. Soc.*, **46**, 374-76 (1963).
9. C.J. Keattch and D. Dollimore, *An Introduction to Thermogravimetry*, 2nd edn., Heyden (London), 57-82, 1975.
10. H.S. Ray, *Kinetics of Metallurgical Reactions*, Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, 39-41, 1993.
11. A.K. Tripathy, H.S. Ray and P.K. Patnaik, *Trans. Instn. Min. Metall.*, **103**, C147-151 (1994).
12. A.Bergholm, *Trans. Met. Soc. of AIME*, **221**, 1121-1129 (1961).
13. D.K. Bose, Studies on Pyrometallurgical Processing of Zirconium Resource, Ph.D. thesis, Bombay University, (1993).