STUDY THE KINETIC OF RECOVERY OF VANADIUM FROM OIL FIRED POWER STATIONS

A Thesis Submitted to the College of Engineering of Nahrain University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

By

Rana Khalid Obaid

B. Sc. in 2004

Moharam	1429
January	2008

Certification

We certify that this thesis entitled “Study the Kinetic of Recovery of Vanadium from Oil Fired Power Stations” was prepared by Rana Khalid Obaid under our supervision at Nahrain University / College of Engineering in partial fulfillment of the requirement for the degree of Master of Science in Chemical Engineering.

Signature: J. Shanshool	Signature: Kh. Al-Mousa
Name: **Prof. Dr. Jaber Shanshool**	Name: **Dr. Khalid M. Mosa**
Date: / /	Date: / /

Signature:
Name: **Prof. Dr. Qasim J. Slaiman**
(Head of Department)
Date: / /

Certificate

We certify, as an examining committee, that we have read this thesis entitled **“STUDY THE KINETIC OF RECOVERY OF VANADIUM FROM OIL FIRED POWER STATIONS”**, examined the student **Rana Khalid Obaid** in its content and found it meets the standard of thesis for the degree of Master of Science in Chemical Engineering.

Signature: J. Shanshool
Name: *Prof. Dr. Jaber Shanshool*
(Supervisor)
Date: / /

Signature: Kh-AL-Mousa
Name: *Dr. Kh. M. Mousa*
(Supervisor)
Date: / /

Signature:
Name: Ass. Prof. Dr. Malek M. Mohammed
(Member)
Date: / /

Signature:
Name: Dr. Basim O. Hasan
(Member)
Date: / /

Signature: A.K-Mohamed
Name: Prof. Dr. Abdul Halim A-K Mohammed
(Chairman)
Date: / /

Approval of the College of Engineering
Signature: M.J. Jweeg
Name: Prof. Dr. Muhsin J. Jweeg
(Acting Dean)
Date: 17/6/2008

Abstract

In this work, it was attempted to study the kinetic of vanadium recovery from fly ash residue by leaching with NaOH solution from previous work of Mosa (1999).

The selected data was chosen when particle size of fly ash were 125, 150 and 200 μm, temperature 343, 353 and 373 K, reaction (leaching) time from 1 to 8 hours and at almost constant concentration of NaOH solution (molarity 3, 3.5 and 4 M).

The results showed that vanadium recovery increased with time and temperature and decreased with particle size.

A second degree polynomial mathematical correlation was employed to describe vanadium recovery response. The correlation coefficient of the obtained correlation was 0.9990 and variance of 0.9981 with confidence levels of 95 %.

Kinetic study showed that the chemical reaction was the controlling step which had the highest resistance among other steps and estimated time for complete conversion of vanadium was about 7 hours. The chemical reaction order was found equals to -3 with activation energy of 1080 J/ mole and frequency factor of about 2.6884.

List of Contents

Variable Notation

Variable	Notation
C_A, C_B	Concentration of reactant, mole/m^3
C_{Ao}	Initial concentration of component A, mole/m^3
De	Effective diffusivity, m^2/s
k_g	Mass transfer coefficient, m/s
k	Reaction rate constant, s
N_A, N_B	Number of moles of component A and B at any time
Q	Rate of mass transfer, mole/m^3 s
ρ_B	Molar density, mole/m^3
R	Radius, µm
r_c	Radius of unreacted core, µm
A_o	Frequency factor
E	Activation energy, J/mole
Q_A	Flux of A through the surface at any radius (r), mole/m^3 s
Q_{AS}	Flux of A through the exterior surface of particle, mole/m^3 s
Q_{AC}	Flux of A through the reaction surface, mole/m^3 s

Abbreviations

TBP	Tri-n-butyl phosphate
D2EHPA	Di(2-ethylhexa) phosphoric acid

List of Figures

List of Tables

CHAPTER ONE
INTRODUCTION

Vanadium is widely distributed metal thorough out the earth crust and this makes it more abundant that such important metal as copper, zinc, lead and tin [Ressel et al., 2005].

Vanadium occurs in carbon containing deposits such as crude oil, coal, oil shale and tar sands, it also could be found in soot ash that occurs as by product at the gasification of heavy petroleum fraction or crude oil resides at the production of synthetic gas [Vanadium, 2003].

Vanadium can exist in different oxidation states from 0 to +5 but the forms found in natural environment are +3, +4 and +5. Oxidation state +4 is the most stable.

During the burning of fuel oils in boilers and furnaces, the vanadium is left behind as vanadium pentoxide (V_2O_5) in the solid residues, sot, boiler scale and fly ash. Vanadium pentoxide is used as the catalyst for a variety of gas-phase oxidation processes.

Vanadium pentoxide is the most common commercial form of vanadium that is dissolves in water and acids forming vanadates [Dashash et al., 1988].

Vanadium has a very low and non-accumulative toxicity; recovery plants can be operated in such manner to ensure no air pollution results [Kirk and Othmer, 1983].

In Iraq, the fuel oil used in electric power stations releases off combustion gases which contain vanadium that could constitute good source of this metal [Jalhoom et al., 1992].

Recovery of vanadium can be achieved by extraction with acids or alkalines from scales and ashes or it could be recovered by amine solvent extraction from ores and slag.

1.1 Vanadium Properties

Vanadium is a rare, soft, ductile grey-white element found combined in different minerals and used mainly to produce certain alloys. It resists corrosion due to protective film of oxide on surface [Vanadium, 2003].

The complexity of constitution, the varying vanadium contents and the wide variety of the vanadium compounds found even in single source make vanadium quite different from many other metals [Ressel et al., 2005].

Vanadium is indeed a 20th century miracle metal. As mankind strives to make products stronger, lighter and softer and more fuel efficient there will be ever increasing demand for the metal one the need for significant increases in sustain table, cost effective vanadium production [Tamlin and Smith, 2007].

1.2 Vanadium Uses

Vanadium has many and continuously increasing industrial uses. Its about 85% of the world production of vanadium is consumed in carbon and stainless steel production, as an alloying agent to produce ferro-vanadium. Vanadium significantly increasing the strength and improves the toughness and ductility of carbon steel used for constructing bridges and pipeline [Judd et al., 1986].

Most of the vanadium produced is used as ferro vanadium or as steel additive. Mixed with alumini in titanium alloys is used in jet engines and high speed-air frames, steel alloys are used in axles, crank shafts, gears and other critical components [Vanadium, 2003].

Vanadium alloys are also used in nuclear reactors because vanadium has low neutron adsorption abilities and it doesn’t deform in creeping under high temperatures [Vanadium, 2003].

Vanadium is used widely in metallurgy, the atomic energy industry, space technology, pharmaceutical industrial processes, and other high-tech industries, making vanadium one of the most important metals for modern technology. In addition vanadium assumes an exceptional position among bimetals in that both its anionic and cationic forms can participate in biological processes, serving as a competitive substrate with phosphate, thereby inhibiting and/or stimulating many phosphate-metabolizing enzymes [Anderson, 2004].

In medicine, vanadium compounds have been used in minute amounts to achieve diverse therapeutic effects. The element must, however be present as stable natural compound with a minimum of toxicity. Medical implants often contain vanadium alloys because of their excellent stability [Wills, 2002].

Vanadium compounds are employed to prepare catalysts such as hydrocarbon oxidation catalyst and catalysts for the manufacture of sulfuric acid [Khorfon et al., 200].

Vanadium has also important applications such as in dyeing industries, glass making and medical chemistry [Krik and Othmer, 1983].

The aim of the work will discussed the explanation of previous experimental data of vanadium recovery from reaction of ash residue (fly ash) from South Baghdad Power Station (in Durah) with sodium hydroxide (NaOH) solution, such as determining of the controlling step and study the reaction kinetic model to find the order and activation energy.

CHAPTER TWO
LITERATURE SURVEY

2.1 Vanadium and its Sources

Vanadium is a metal contaminate that is present in most crude oils in an oil-soluble forms and the levels found in residual fuels depend mainly on the crude oil source [Hobson, 1979].

The atomic number is 23, atomic mass 50.9414 g/mol. Electronegativity according to Pauling 1.6, density 6.1 g/cm^3 at 20° C melting point 1910° C, boiling point 3407° C, Vander Waals radius 0.124 nm isotopes 5, electronic shell (Ar) 3d^3 4S^2, energy of first ionization 649.1 kJ/mol, Discovered by Nils Sefstrom in 1830.

Vanadium is widely distributed throughout the earth crust abundance of 135 ppm. This, in fact, makes it more abundant than important common metals such as copper, zinc, lead and tin [Ressel et al., 2005].

The primary source of vanadium is titanomagnetite deposits in which vanadium is present as a minor replacement for iron [Anderson et al., 2004].

There are many sources of vanadium to be considered as follows:

a. Vanadium occurs in carbon containing deposits such as crude oil, coal, oil shale and tar sands [Vanadium, 2003]
b. Vanadium is also found in soot ash that occurs as a byproduct of the gasification of heavy petroleum oil fraction or crude oil residues at the production of e.g. synthesis gas [Vanadium, 2003]. The vanadium concentration in oils varies greatly depending on their origin. In crude oil it ranges from 3 to 260 ppm and in residual fuel oil from 0.2 to 160 ppm [Costigan, 2001].
c. Vanadium is also a trace element in fossilized organic matters such as carbonaceous fossils and can be found in uranium-bearing minerals [Anderson et al., 2004].

However, minerals deposits in Vanadium occur as a major constituent are very rare. It occurs almost in variably as a minor constituent in primary source of other elements. Generally, vanadium supplies have mainly been derived as a byproduct of other elements [Ressel et al., 2005].

Various vanadium ores are known but none is mined as such for the metal, which is generally obtained as byproducts of other ores [Perron, 2001].

Vanadium is never found unbound in nature. It occurs in about 65 minerals among which are patronite, vanodinite, carnotite and bauxite [Vanadium, 2003].

Vanadium is also found in soil where the contents of soil are related to those of the parent rocks from which they are formed and range from 3 to 310 ppm. The highest concentration is found in shale and clays. Vanadium is evenly distributed in the soil horizons, but there is sometimes a higher level in the horizon, possible connected with the vital activity of plants. It present in the soil of France, Japan, Spain, United Kingdom and United States of America at levels that are partly determined by the distribution of iron in these soils, levels range from 1000 to 68000 ppm. The lowest concentration was reported from Japan and the highest from Spain [Dashash et al., 1988].

Vanadium can also be found in water. The level of vanadium in water in different parts of the world varies from undetectable to 0.22 ppm [Dashash et al., 1988].

Natural source of airborne vanadium are marine aerosols and continental dust. The concentration of vanadium in air at the South Pole is very low (0.001-0.002 ppm). Only small amounts of air borne vanadium are produces as a result of volcanic action [Zoller et al., 1973].

Vanadium occurs in small amounts in all plants usually at concentration of few ppm dry weight. Within a given species, variation is influenced by soil-vanadium levels, soil acidity and growing conditions, but the range of variation is not large. Mean concentration of analyzed vanadium in 62 plant species analyzed, is about 0.16 ppm for fresh weight plants to 1 ppm for woody plants. Vanadium also appears to be present in all animals, but tissue levels in most vertebrates are so low makes that detection difficult. Higher concentration has been found in marine species, especially invertebrates [Tyler, 1970].

Petroleum contains vanadium and a number of other metals at low concentration. Among them are 0.1-1.0 ppm Ba, Mn, Zr, Sr, Pb, Mo, Li, and 1.0-10 ppm Al, Mg, K, Sn and 10-100 ppm Cu, Ni, V, Fe, Na.

These metallic impurities cause problem in the treatment of crude oil such as corrosion which takes place in pipelines.

The fuel oil used in the oil-fired electric power station has relatively high content of vanadium and other metals such as nickel.

The content of vanadium in Iraqi crude oil is associated with its density (being of the order of 200 ppm in the heavy Gayyarra oil and about 30 ppm in the lighter more economically important oil).

The fuel oil used in electric power stations releases ash, which contain large quantities of vanadium that could constitute a major source of this metal.

In Al-Musaiab power station for example, the feed fuel oil is expected to contain about 100-10 ppm vanadium when heavy oil is used at the rate of 4500 ton/day. This means a release of 300-400 kg of vanadium/day [Barbooti and Al-Madfai, 1988].

Table 2.1 gives the results of element analysis of samples taken from scale and ash residues in the South of Baghdad power station. These results indicate the high vanadium concentration in the scale residues is higher than any one of the known vanadium ores [Jalhoom, 1992].

Table 2.1 Ash residues analysis from South Baghdad Power Station [Jalhoom, 1992]

Residue	V%	Ni%	Fe%	Na%
Scale	24.0	6	1.49	2.8
Ash	3.5	5	1.8	0.8

A Swedish process has been designed to recover vanadium from oil fired power station residues.

An extraction plant has been in operating with capacity of 2000 tons of ash per year, corresponding to about 100 tons of vanadium [5% contents].

The solvent extraction of vanadium was perfumed with 20% DEHPA and 15% TBP in three small-scale mixer-settler stages.

The recovery of vanadium has also been examined in Japan, using hydrochloric acid leaching, which showed the best extraction capability for vanadium and other metals in the oil fired boiler slag. As a result 94% of vanadium in the oil-fired boiler slag was recovered in pure solution form [Izumi et al., 1987].

Recovery of vanadium and nickel in fly ash from heavy oil has also been studied in Japan with a two step leaching process [Akita et al., 1995].

In the leaching process, nickel is dissolved with NH_4Cl in the first step, followed by vanadium leaching with Na_2CO_3.

2.2 Vanadium Oxides

Vanadium can exist in different oxidation states from -2 to +5, but the forms found in the natural environment are +3, +4 and +5. Oxidation state +4 is the most stable [Anderson, 2004].

During the burning of fuel oils in boilers and furnaces, the vanadium is left behind as vanadium pentoxide (V_2O_5) in the solid residues, soot, boiler scale and fly ash. Vanadium pentoxide is used as the catalyst for a variety of gas-phase oxidation processes. The most frequently used vanadium pentoxide catalyst contains 4-6% vanadium as vanadium pentoxide as silica base. It is the most commonly used vanadium compound and exists in the pentavelent states as yello-red or green crystalline powder of relative molecular mass 181.9 [Costagin et al., 2001].

V_2O_5 is used in metallic anhydride and in a making ceramics. It is added to glass to produce green or blow tint [Vanadium, 2003].

Vanadium pentoxide [V_2O_5] is the most common commercial form of vanadium, it dissolves in water and acids and form vanadates with bases [Dashash et al., 1988], and it widely used in the conversion of naphthalene to phthalic anhydride. It is also used as catalyst in the process of CO_2 removed from gas mixture in ammonia synthesis [Colton and Wilkinson, 1988].

It also can be used as coloring agent and provide ultraviolet filtering properties in some glasses [Costigan et al., 2001].

Vanadium in the +3 oxidation state V_2O_3 is basic and dissolves in acid forming a green hexa-aquaion V^{+3} salts which are strong reducing agents [Dashash et al., 1988].

Vanadium in the +2 oxidation state VO_2 is used in the glass coating that can block infra red radiation at some specific temperature [Dashash et al., 1988].

Other forms of vanadium in +5 oxidation state are the vanadate ion $[VO^-_3]$ and include ammonium meta vanadate (NH_4VO3), sodium metavanadate ($NaVO_3$) and sodium orthovanadate (Na_3VO_4) [Costigan et al., 2001].

Compounds in the +4 oxidation state are derived from the vanadyl ion (VO^{+2}) for example, vanadyl dichloride ($VOCl_2$) and Vanadyl sulfate ($VOSO_4$).

Vanadium $^{+5}$ (V^{+5}) is reduced to V^{+4} by relatively mild reducing agents. Nearly all of the complexes of V^{+4} are derived from the vanadyl ion (VO^{+2}). Most of those complexes are anionic and few are non-electolytes. Vanadium in this oxidation state forms a large number of five or six coordinate complexes, such as vanadyl acetylacetonate and vanadyl prophyrins found in crude petroleum.

Pure V_2O_5 melts at 660°C and therefore has an amphoterons character, where as lower oxides show basic reactions, which increase in strength with decrease of oxidation coefficient. VO_2 melts at 1642°C and V_2O_3 at 1977°C [Ressel et al., 2005].

2.3 Recovery of Vanadium

2.3.1 Recovery of Vanadium from Iron and Steel Making Process [Lindrall, 2006]

The best available technology for vanadium recovery from iron and steel making processes is based on pre-oxidation of hot metal from iron-making prior to the decarburization step. The four most dominating processes are: Highveld process, The Pan-Steel process, The NTMK-Duplex process and The New Zealand steel vanadium recovery process.

The four processes basically shave the same chemical and process principles. The main difference between the processes is the type of reactor and the initial V-content in the hot metal due to different V-content in iron ores.

Vanadium oxidized by oxygen to a slag phase. This slag is called V-slag or V-spinal slag. One main drawback with V-slag produced from pre-oxidation of hot metal is that it can not be used directly for FeV production due to the high Fe-content and relatively low V-content. Therefore, it is most commonly used as raw material for vanadium extraction.

2.3.1.1 The Highveld Process [Gupta and Krishnamurthy, 1922]

Highveld steel vanadium process is the biggest producer of V-slag, for further processing to V_2O_5 (vanadium extraction) and ferrovanadium alloys. The Highveld process for vanadium recovery from hot metal is described in Figure 2.1.

A titaniferrous magnetite type of ore containing 1.65% V_2O_5 is used as raw material. The hot metal is produced by pre-reduction in a rotary kiln followed by melting in submerged arc furnace. The V-content in hot metal is as high as 1.2%, to achieve a high rate of vanadium oxidation and low rate of carbon oxidation the shaking ladle has a working temperature around 1400° C. Steel scrap, mill scale, anthracite and oxygen is added producing a V-slag with about 24% V_2O_5. Mill scrap and anthracite are added during the oxygen blow to control temperature and the carbon content of the bath.

The slag is crashed and lumps of iron are removed with an overhead magnet. Slag fines are separated from coarse slag [6-32 mm] by screening. Figure 2.2 shows a schematic drawing for this process.

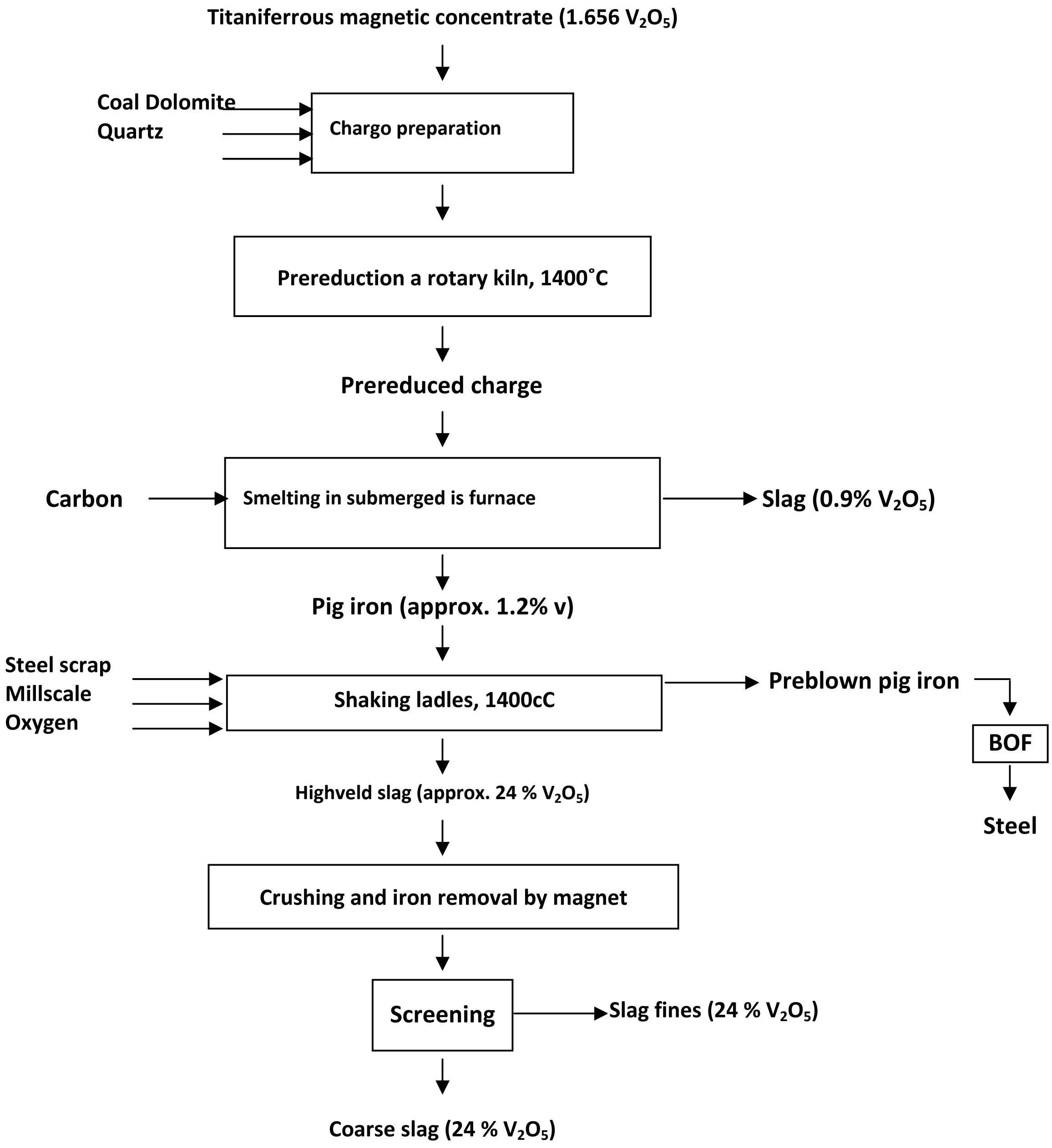

Fig. 2.1 Pyrometallurgical V-recovery process at Highveld Steel [Gupta and Krishnamurthy, 1922]

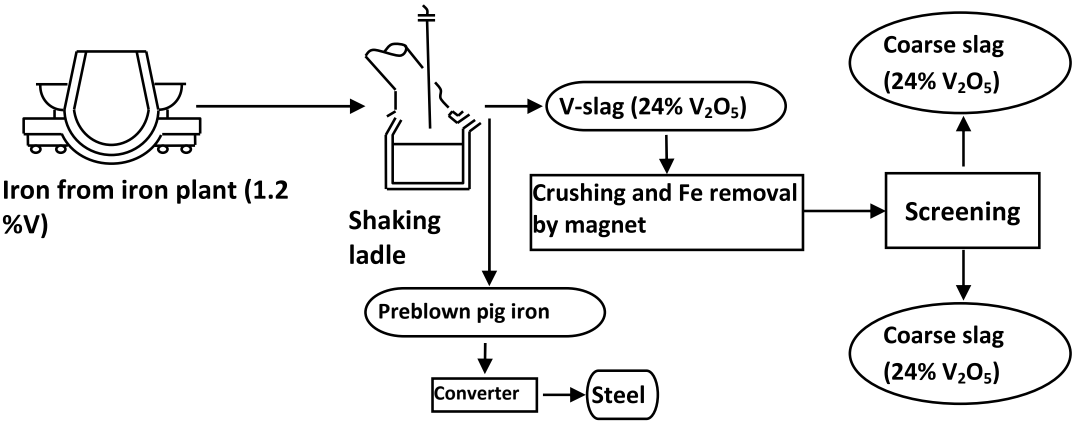

Fig. 2.2 Highveld-steel V-recovery process [Gupta and Krishnamurthy, 1922]

2.3.1.2 The New Zealand Steel Vanadium Recovery Process [Guozhu, 2006]

The iron making process is very much like the Highveld process. Pre-reduction in rotary kilns and final reduction in submerged arc furnace.

The V-content in the hot metal is 0.42%. The vanadium recovery step is carried out in a transfer ladle before the decarburization step with oxygen as oxidant [Ye, Guozhu, 2006].

2.3.1.3 The NTMK-Duplex Process [Guozhu, 2006]

The pre-oxidation of vanadium in hot metal is made in a ladle at comparatively low temperature. Mill scale, scrap and vanadium bearing pellets are added as coolants. Oxygen is used as oxidant. One increasing feature of the process is that the V-slag remains in the pre-oxidation converter for three cycles before it is tapped; producing a V-slag with 16-

28% V_2O_5 and a vanadium recovery of 85%. Figure 2.3 has a pig iron analysis approximately according to Table 2.2.

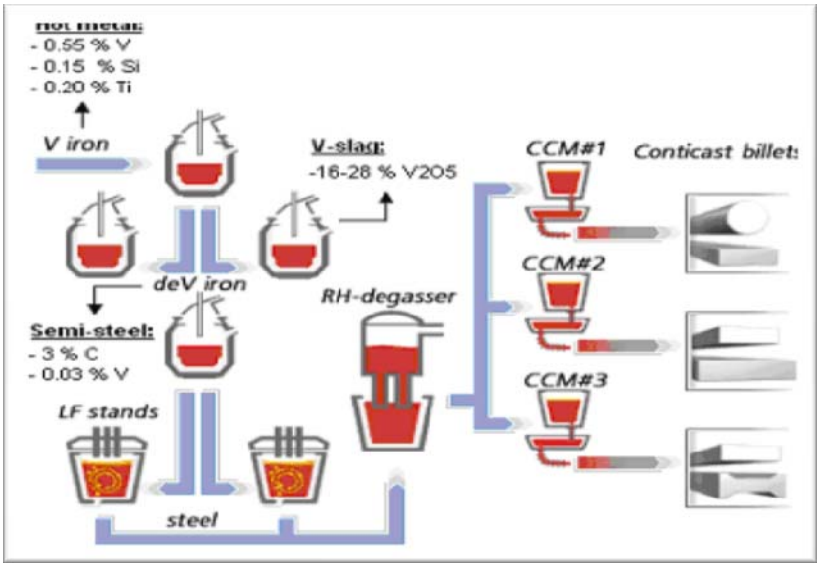

Fig. 2.3 The NTMK V-recovery Process [Guozhu, 2006]

Table 2.2 Hot metal compositions for the three major V-producing countries and at SSAB [Guozhu, 2006]

Country	Composition of hot metal in [%]						
	C	V	Si	Mn	P	S	Ti
S. Africa [Highveld]	3.95	1.1	0.24	0.22	0.08	0.037	0.22
Russia [NTMK]	4.2-4.7	0.4-0.5	0.17	0.26	0.05	0.032	0.08-0.17
China [Pan-Steel]	4.5	0.37	0.2	0.21	0.05	0.05	0.12
Sweden [SSAB]	4.4	0.3	0.35	0.4	0.035	0.05	–

2.3.1.4 The Pan-Steel Process [Guozhu, 2006]

The titanium iron is melted in a blast furnace producing a pig iron with a composition according to Table 2.2. The reactor in this case is similar to a normal LD-converter.

The V/P-ratios in the hot metal and in the V-slag are 3.75 and 2000 respectively. A flow sheet of the Pan-Steel V-recovery is shown in Figure 2.4.

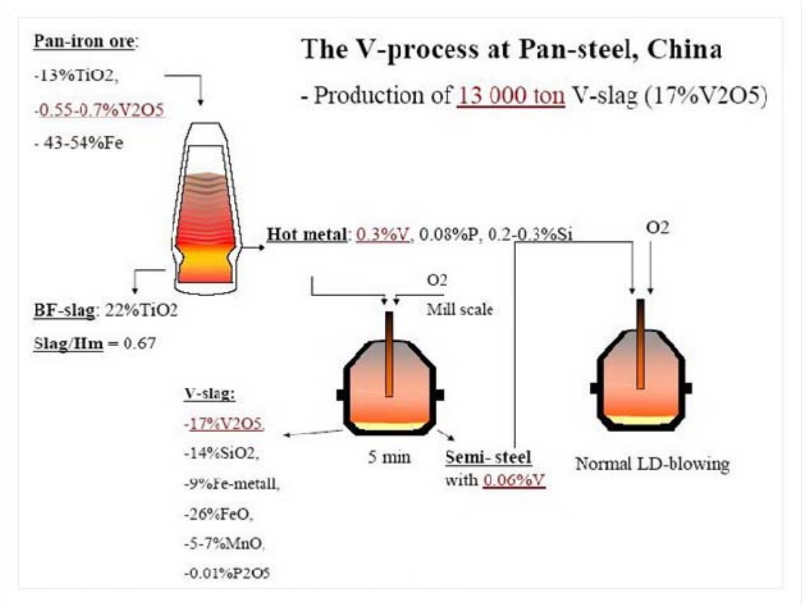

Fig. 2.4 Pan-steel V-recovery process [Guozhu, 2006]

2.3.2 Recovery of Vanadium from Residues and Catalysts [Tamlin and Smith, 2007]

Vanadium catalysts used in petrochemical and chemical industries can be processed to remove the vanadium and other deposited metals, once they have reached the end of their useful life.

The burning of vanadium-containing fuel oil precedes a fly ash containing vanadium which can be treated. Cool stone provides another source of vanadium raw materials. Processing many of this material is usually complex and costly. A number of small, high cost, high polluting processes of spent catalyst and oil residues as well as small mines have sprung up to capitalize on vanadium prices that allowed high coast production to be profitable.

2.3.3 Process for the High-Yield Recovering of Vanadium from Petroleum Combustion Residues [Corigliano et al., 1989]

a) A process for recovering vanadium from solid residues of combustion of petroleum fractions consisting of treating residues with a saturated aqueous solution of sodium hydroxide (in a ratio of 3-5 moles of NaOH per mole of vanadium) where by the residues become wetted, drying and roasting the so treated residues at 100-250°C, leaching with water thereby obtaining an alkaline solution containing vanadium selectively extracted from said residues with a yield of at least 80%.

b) According to the above process the vanadium extracted in alkaline solution is recovered by bringing the solution to a pH ranging from 1.7 to 2.3 by the addition of sulfuric acid and by adding ammonium salt in an amount of 60-80 g/l and subjecting the solution to digestion at 70-100°C for 20-40 minutes.

According to (a) the staring residues are leached with sodium hydroxide solution having a concentration of 5-15% by weight in the presence of oxiding agents. It is possible to use hydrogen peroxide or preferably aqueous sodium hypochlorite as an oxidizer. Advantageously, an amount of oxidizing agent ranging from stoichio metric value up to 100% in excess with respect to the vanadium (IV) and iron (II) contents of residues, and a quantity of 3-5 liters of sodium hydroxide per kg of solids (Starting residues) are used.

The alkaline leaching and oxidizing steps can be performed together in a similar reactor kept under stirring and heated up to 60-80°C for a period ranging from 30 minutes to few hours.

According to (b) the starting residues are mixed with a saturated solution of sodium hydroxide, in an amount of 3-5 times [mole/mole] that of the vanadium, then they are dried and roasted in dry air at 100-250°C and finally leached with water in the ratio of at least 5 l/kg of residues the leaching solution according to (a) or (b) containing 80-95% of the vanadium contained in the starting solids. After being filtered and washed, the collusion is made acidic (pH of approximately 2) with sulfuric acid and an ammonium salt is added to precipitate the vanadium as ammonium polyvanadate. For this purpose, ammonium sulfate can be used in the amount of 60-80 g per liter of acidified lixiviate, heating to 70-100° C. The ammonium polyvanadte is then subject to mild calcinations at 180-200° C to obtain vanadium pentoxid, which is commercially valuable product, and ammonia. The latter can be collected in sulfuric acid to be recycled to the ammonium polyvanadate precipitation step. From this, the proposed aim and object can achieve. The advantages can be achieved economically even for petroleum combustion residues with low vanadium content.

Abdu-Al-Barry [1966] showed that the recovery of vanadium from the residues of the burning of fuel oil in Iraqi oil-fired electric power station can be done by leaching the residues with sulfuric acid. The vanadium (IV) was extracted into kerosene solutions of DEHPA and TOPO. Two stages of leaching followed by n stages of extraction have been used. Vanadium was precipitated from strip solution with ammonium hydroxide. This was calcined to the final product V_2O_5 [Al-Duhan, 1996].

Mosa [1999] studied the recovery of vanadium from scale and ash residues of some Iraqi oil-fired power station where a pilot plant has been designed and installed at Ibn-Cina company site Tarmiya. The plant utilizes the following processes:

1. Leaching with NaOH solution at a bout 95°C according to the following equation

$$\mathbf{V_2O_5 + 2NaOH \rightarrow 2NaVO_3 + H_2O}$$

2. Filtration of the leach solution
3. Precipitation of ammonium metavanadate NH_4VO_3 using ammonia solution according to this equation:

$$\mathbf{NaVO_3 + NH_4OH \rightarrow NH_4VO_3 + NaOH}$$

4. Calcination of ammonium metavanadate in presence of oxygen to produce vanadium perntoxide as in the following equation:

$$\mathbf{2NH_4VO_3 \xrightarrow{Heat} V_2O_5 + 2NH_3 + H_2O}$$

Figure 2.5 shows this process

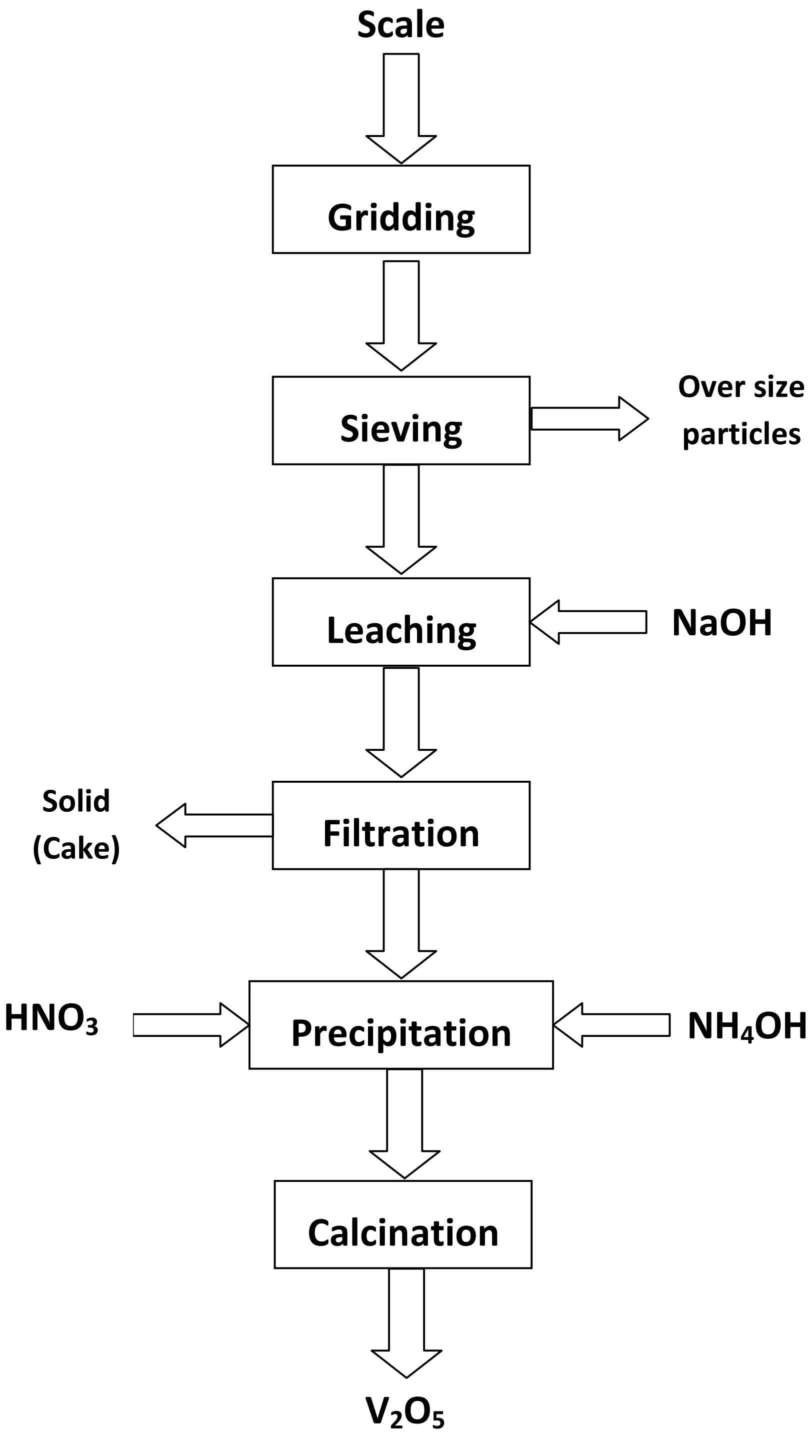

Fig. 2.5 Block Diagram of Vanadium Recovery by Alkaline in Ibn-Cina (Mousa, 1999)

The effects of available process viz. temp., particle size of scale, molarities of sodium hydroxide and the leaching time on the percentage of vanadium recovery were investigated. And it was found that the percentage of vanadium recovery increased with:

I. Increasing temperature
II. Decreasing dp
III. Increasing molarities of NaOH.
IV. Increasing leaching time.

These processes are applicable to various types of residues such as ash, soot, crusts, aqueous or sulfuric lixiviates of ash and soot, water correction mud, etc. The vanadium content in such residues can be as low as 2-3% and the contents of further interfering cations as iron, calcium, magnesium, etc.

2.3.4 Recovering of Vanadium from Petroleum Coke as Dust [Malone et al., 2001]

Many heavy crudes contain significant amounts of vanadium and sulfur with lesser amounts of nickel, iron and other metal compounds. Many cokers produce coke which is contaminated with metals. Such materials have enough vanadium to cause processing problems but vanadium concentration is too low to make vanadium recovery economically attractive. Vanadium in petroleum containing coke is difficult to recover directly, because it is in a form which dose not lends itself to conventional leaching approaches. Vanadium in coke can be recovered much more readily after combustion, because vanadium in the ash produced is more susceptible to leaching, though even here some treatment such as sodium carbonate or sodium hydroxide was needed to improve metal [Fe] recovery during leaching. The best way to recover vanadium in coke is to use special form of molten metal (Fe) processing to dissolve the carbon and vanadium. The carbon, probably present in the form of collapsed metalo-porphyrin surrounding an atom of vanadium metal, dissolved readily in the molten iron bath, freeing the vanadium and permitting rapid and complete dissolution of the vanadium metal in the molten iron bath. The net production of vanadium is then removed from the bath as “dust” which could be either an oxidized form of vanadium or iron/vanadium metal, depending on the oxidation conditions in the bath. The process is fast and simple. No special processing of the coke was needed, and it did not require dry coke, but could tolerate and even benefit from the presence of some water in the coke. Heat/utility requirements were low, in fact the worse the feed in terms of % vanadium in the coke, the more heat the process generated per weight of vanadium recovered. The process was tolerant of many other impurities found in coke containing fed, such as nickel and sulfur compounds.

2.3.5 Recovery of Vanadium from scrap Alloys [Menashi et al., 1981]

This process is directed to selectively removing and subsequently recovering vanadium from a mixed solid precipitate containing alkaline earth metal vanadate, typically calcium vanadate, and one or both tungastate and molbdate. The alkaline earth metal vanadate can be partitioned from such mixed solids by treatment with an aqueous carbonic acid solution having a superatmospheric pressure or an aqueous formic acid solution. After separation of the sold and liquid phases, vanadium is recovered from the aqueous phase by boiling of water to precipitate a product (Optionally with the addition of CaO) or by solvent extraction.

When formic acid solution is used in the partition, the vanadium is dissolved. The vanadium is then stripped by neutralizing the solution with CaO or $Ca(OH)_2$ to precipitate a CaO product. The overall processing system disclosed here is that the mixed solid can be produced by treating a pregnant liquor contain Cr^{+6}, Mo^{+6}, V^{+5} and W^{+6} values with calcium ions and subsequently reduction the Cr^{+6} values to Cr^{+3} with formate ions.

Accordingly, the spent liquor containing calcium formate can be recycled to the V^{+5}, W^{+6} and Mo^{+6} precipitation stage where it is Ca^{+2} content is used to precipitate additional metal values and its formate ion content is ultimately used to reduce Cr.

An important aspect of the process is that all solutions are recycled. Thus, no aqueous effluents are involved and incomplete recovery of vanadium dose not represents a loss. The carbonic acid dissolution of the mixed solids results in removal of about 80% of the vanadium values and the product is low in Mo^{+6}, W^{+6} contamination.

In contrast, the formic acid dissolution step recovers in excess of 90% of the vanadium, but the resulting precipitated product contains a higher Mo and W impurity concentration. A preferred process involves first treating the mixed solids with carbonic acid to partition and subsequently recover pure vanadium, and after treating the mixed solid residue with a small volume of formic acid to recover additional vanadium values. The format leach solution may then be recycled, and the substantially vanadium-free solid may then be delivered to subsequent Mo and W recovery stages.

The solid calcium cake is contacted with formic or acetic acid. This results in the evolution of CO_2 and in an aqueous phase rich in vanadium as

V^{+5}. After separation of the solid CaMoO, vanadium values may be recovered from the solution by treatment with $Ca(OH)_2$, ammonia, CaO, NaOH and other bases. As the pH rises, vanadium precipitation as a calcium vanadate or ammoniated vanadium produces. Alternatively, the vanadium values may be recovered directly from the said solutions by solvent extraction processes based on the use of extractants such as amines.

This technique has been found to be capable of recovering 90% or more of the vanadium from the cake and results in V^{+5} leach solution typically containing 15 g/L V^{+5} [Menashi et al., 1981].

Another object is to provide vanadium recovery techniques which produce no aqueous effluents and are efficient from the point of view of reagent consumption and reagent cost per unit of vanadium product.

The vanadium recovery process is based on the discovery that the calcium vanadate may be selectively dissolved from a mixed cake also containing MoO and WO ions by treatment with formic acid and/or acetic acid in the pH range of 2-7.

2.3.6 Recovery of Vanadium from Vanadium-Containing Ore [Hansen et al., 1987]

The conventional method for recovering vanadium from vanadium containing ores includes as an initial step the roasting of the vanadium ore with a sodium salt to form roasted products which contain sodium vanadate in solid form. The roasted material is then cooled, crushed, ground and water leached in agitation leach tank in a conventional manner. The solubilized sodium vanadate in solution is recovered from the solids through convential solid-liquid separation such as filtration or counter current decantation.

The latter step generally involves precipitating the vanadium as ammonium metavanadate. In some instances, the filtrate is evaporated after precipitation to recover the sodium salt and to avoid liquid effluent disposal. Recovery methods are sought which is not only enable a high percentage of recovered vanadium but also provide a high grade of leach liquor.

A heap leaching process has been proposed for recovery of various metal values from ores. In the heap leaching process, the ore is placed in a pile and the leaching liquor is placed on top of ore and then seeps through the depth of the pile where by metal values are dissolved in the liquor and the liquor is recovered at the bottom of the pile and treated to recovered the metal values.

This process is conducted to recover at least about 75; say about 80 to 95 percent of the vanadium contained the roasted ore in at least one of the sections of the heap. The rate of leaching solution per unit area of the heap per unit time is often about 50-500 liters per square meter per day. Generally, the leaching solution has a pH of at least about 7.

2.3.7 Recovery of Vanadium from scrubber waste [Friedman, 1986]

Many industries produce waste which contains metals. Some of these metals are toxic and therefore the waste containing them can have hazardous to store. The recovery of vanadium, nickel and iron from waste from stack gas scrubbers includes the following:

a. Filtering the waste

b. Adding a basic material to filtrate produced by step [a] to raise its pH to about 11 causing a precipitate containing iron, vanadium and nickel to from.
c. Dissolving the Fe-V-Ni precipitation in acidic solution having a pH less than about 3.
d. Adding a basic material to the solution to raise its pH to about 3 causing a first vanadium rich precipitate to form and raising its pH to about 6.
e. Separation out the first vanadium rich precipitate from the remaining liquid.
f. Adding a basic material to the remaining liquid from step [e] to raise its pH to about 10 causing a nickel rich precipitate to form then separation out this precipitate from the remaining liquid.

In this process only vanadium in the +4 oxidation state will be recovered, but that will usually be the majority of vanadium present in the waste. Also 86% of vanadium should be recovered of the total vanadium present at purity of about 97%.

A second process is achieved to the recovery of vanadium, nickel includes the following steps:

a. Lowering the pH of the waste to about 0.5.
b. Raising the pH of the waste to about 4-5, causing iron-rich precipitate to form.
c. Separation out the iron-rich precipitate from the waste.
d. Raising the pH of the waste to about 8-10 causing a nickel rich precipitate.
e. Separation out the nickel rich precipitate from the waste.
f. Recovering vanadium from the remaining waste.

This process can achieve a higher degree of vanadium recovery than the previously process, but is also more expensive because of its use of oxidant.

2.3.8 Recovery of Vanadium from Residues [Cole and Spencer, 1970]

According to this process, vanadium containing solids are suspended in a liquid capable of dissolving chlorine and such suspension is treated with chlorine under supper atmospheric pressure. It is found that this enables to vanadium to be converted into the form of volatile vanadium chloride, generally the use of supper atmospheric pressure with this process is more important since, by this means over 99% of the vanadium in the containing solid can be chlorinated and recovered. Suitable pressures are 1.34 to 18 atmospheres preferably 2.36 to 11.20 atmospheres. The chlorination temperature is normally 20-250° C preferably 100-180° C. The suspension to be chlorinated will normally have solid content in the range of 5-60% by weight preferably 10-40% by weight.

2.3.9 Commercial Processes for V-Extraction

Some typical commercial processes are shortly described in the followings:

2.3.9.1 Direct V-Extraction from Titaniferrous Magnetite, the Vantra Process

The vantra process is a typical direct V-extraction process based on direct use of titaniferrous magnetite. The process flow sheet is shown in Figure 2.6.

The vantra process uses a magnetite concentration with 1.65% V_2O_5. This means that the roasting step has to treat also the 98% “no V_2O_5”-fraction and the process generates a large amount of tailings. There are also other variations of the process, but the principle remains the same.

2.3.9.2 Direct V-Recovery from Converter Slag, Talcahuano, Chile

The process flow sheet of the direct V-recovery from converter slag is shown in Figure 2.7 [Cole and Spencer, 1970]. This method is of interest for the MISTRA project since the used converter slag has almost the same chemical composition as the SSAB LD-slag, although this process is no longer in use.

The chemical composition of the slag used is shown in the table below.

V_2O_5	CaO	SiO_2	P_2O_5	Fe	MnO	MgO	Al_2O_3
5.7	47	11	3.2	15	4	2.5	1.2

It has been claimed that V_2O_5 in the slag exists in various calcium vanadates. The purpose of the first process step, pyrite roasting aims at liberating V_2O_5 from the calcium vanadates. The high lime content was thus a major disadvantage since it will consume more pyrite in the roasting step and more sulphuric acid in the subsequent leaching step. Calcium will end in the stable compound, $CaSO_4$.

The biggest problem for this process is that it will generate more solid waste than the treated LD-slag due to the formation of $CaSO_4$.

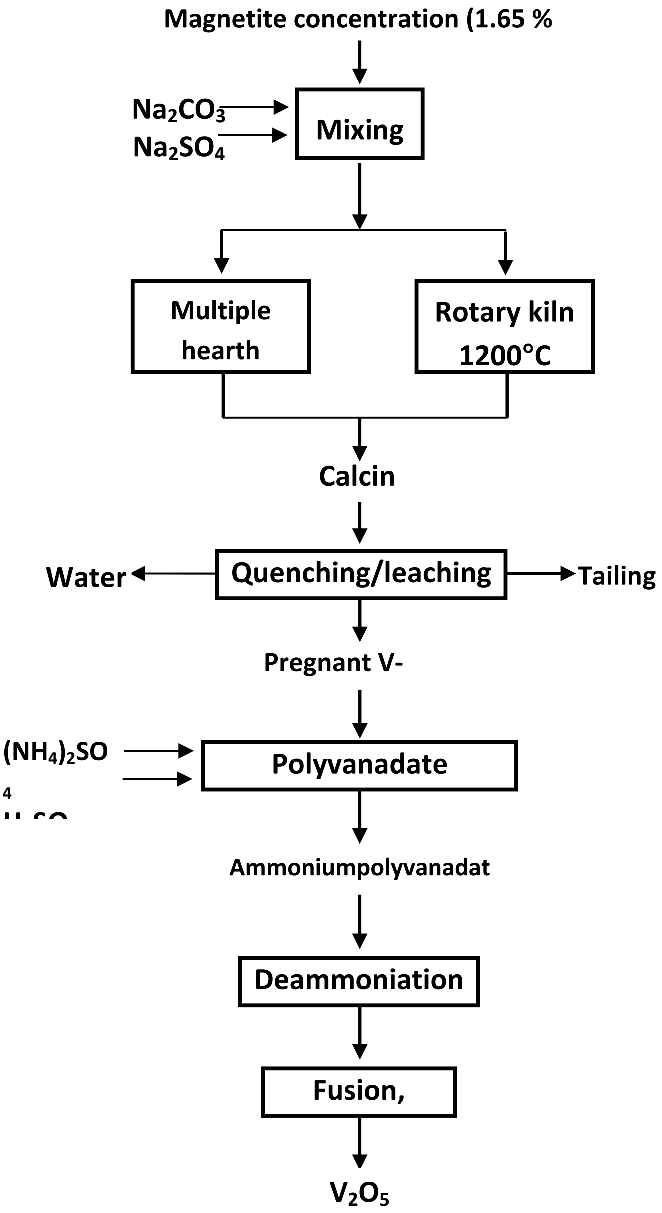

Fig. 2.6 Vanadium extraction by the VANTRA process [Cole and Spencer, 1970]

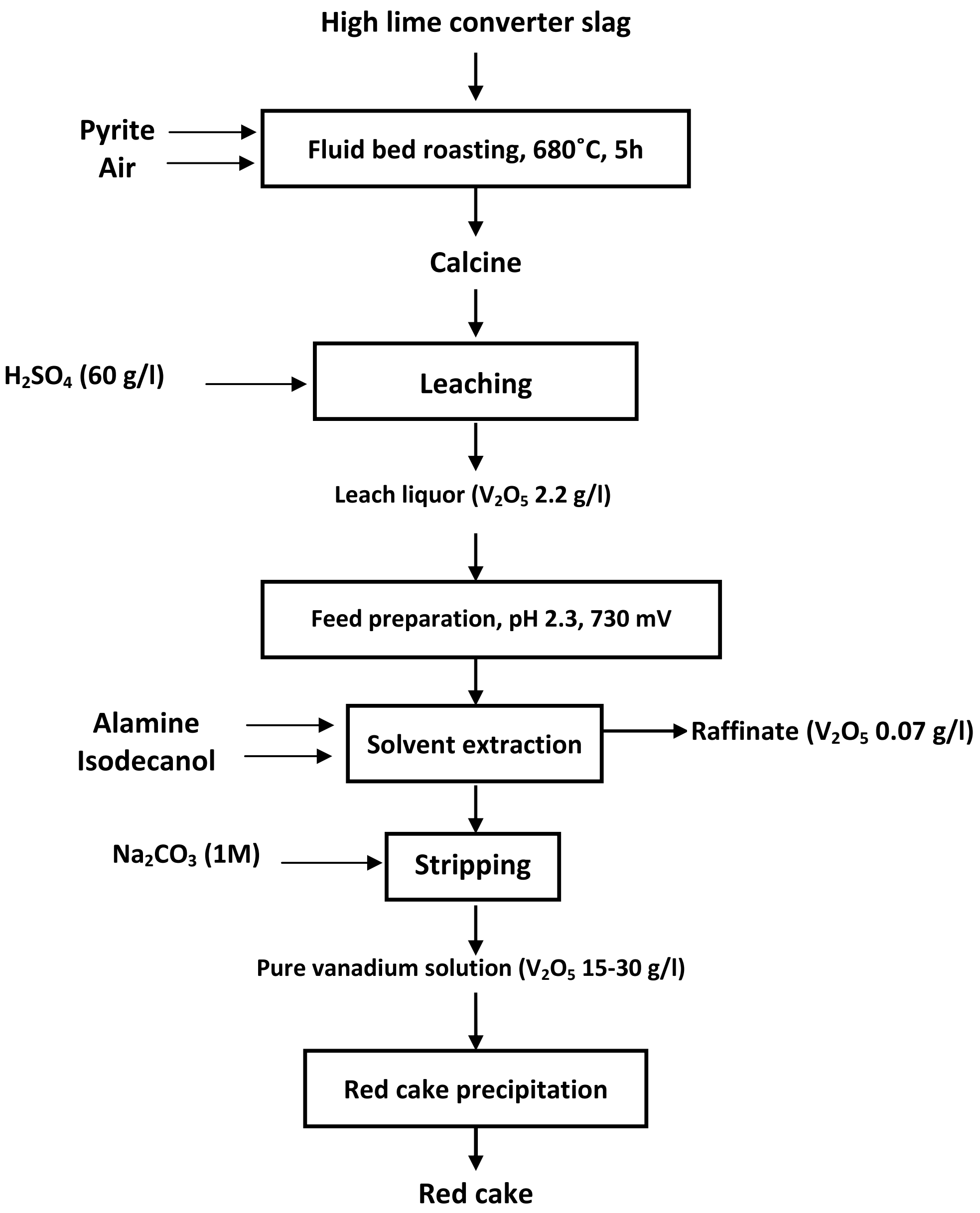

Fig. 2.7 Vanadium extraction from a high lime converter slag [Cole and Spencer, 1970]

2.3.9.3 Processing of Fly and Boiler Ash [Cole and Spencer, 1970]

A quite frequently used V-source is the residue from use of the Venezuelan oil. The vanadium content in the crude oil, residual oil, petroleum coke and finally fuel ash are shown in the table below.

Venezuelan crude oil	150 ppm V
Residual oil	600 ppm V
Coke product [petroleum coke] after concentration	4,000 ppm V
Fuel-ash	15% V_2O_5

The major constituents in the fuel ashes are normally C, V, S, Fe, Ni, aluminosilicates. There are two types of fuel ashes:

- Fly ash: collected in electrostatic filter
- Boiler ash: deposit on the ash pit beneath the flame zone or outside the boiler tube, less amount but higher V-content.

There are both hydrometallurgical processes for V-recovery from the fuel ashes as shown in Figure 2.8.

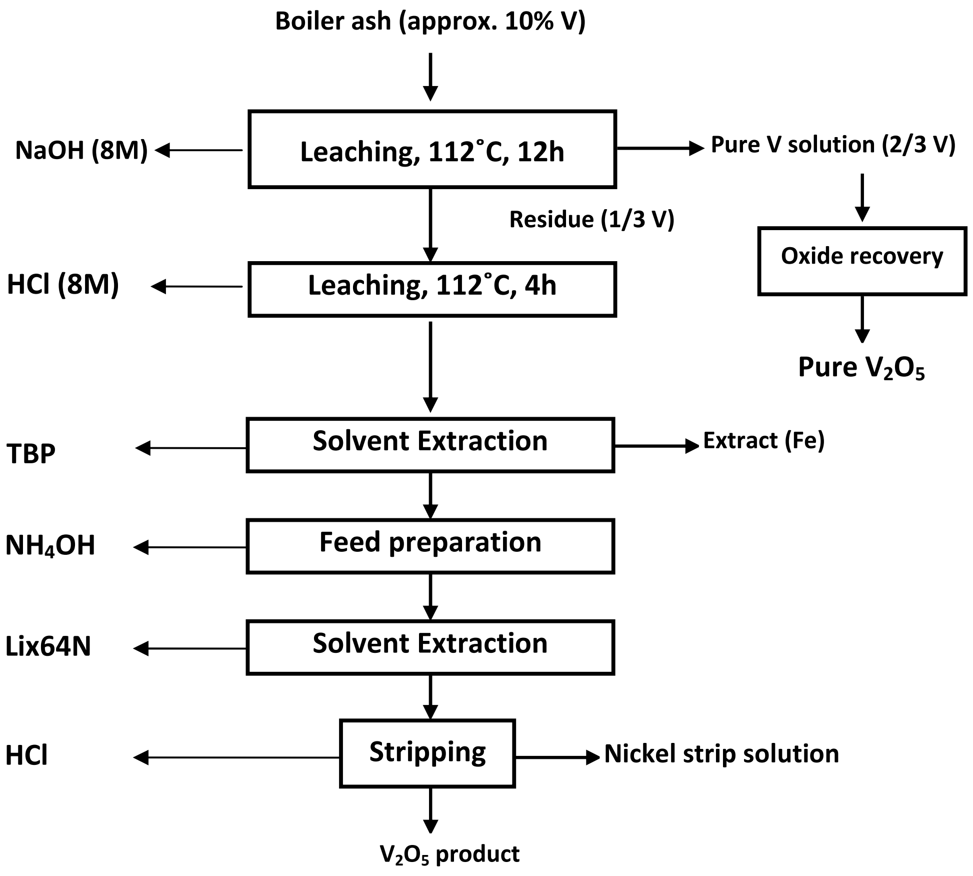

Fig. 2.8 Hydrometallurgical recovery of vanadium from boiler ash [Cole and Spencer, 1970]

2.4 Vanadium Recovery by Leaching

The most common extraction route consists of four process steps: Salt roasting, leaching, solution purification and finally precipitation and V_2O_5 fusion. Direct acid and alkaline leaching is an alternative to salt roasting. However, they are only used in smaller commercial plants treating Uranium-Vanadium ores, catalyst, ash and boiler-residues.

The available vanadium production route by solvent extraction is shown in Figure 2.9.

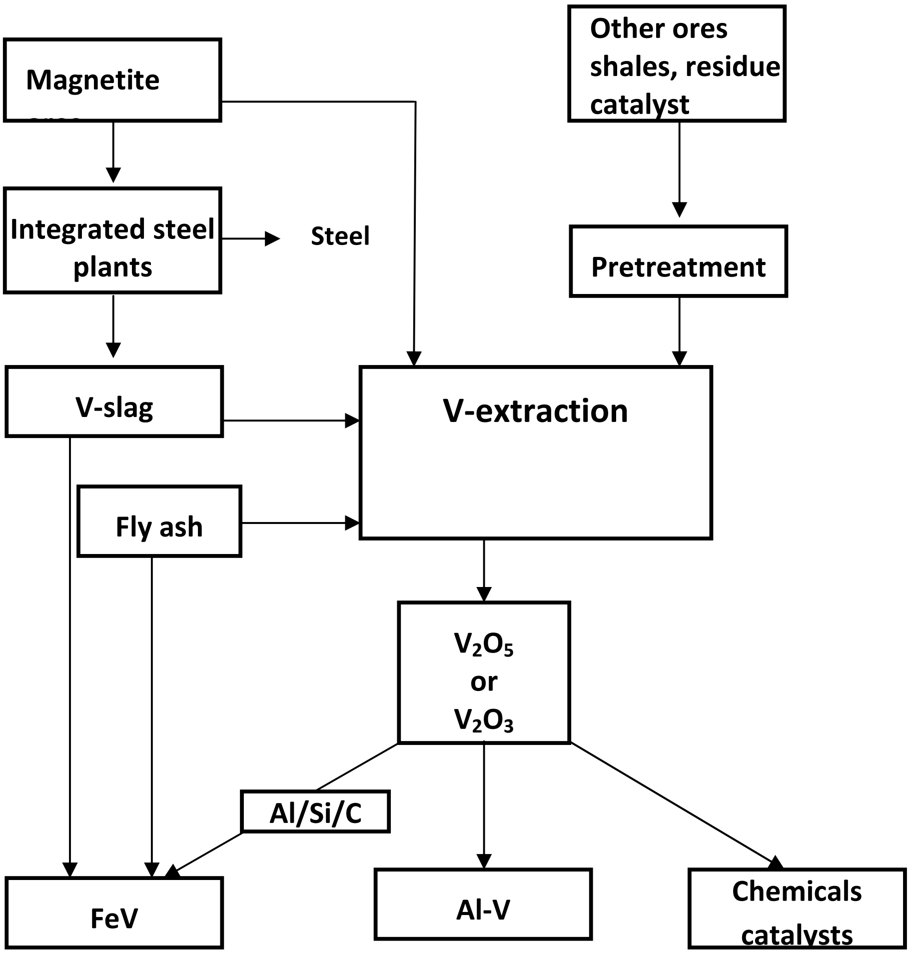

Fig. 2.9 Vanadium production routes

2.4.1 Salt Roasting

The objective with salt roasting is to render the metal-values water-soluble. Soda and Sodium sulfate can be used instead of salt, soda roasting and sulfate roasting respectively. Soda roasting is probably the most used method today due to high environmental requirements. Sodium sulfate is selective but its high operational temperature and high price limit its use.

The roasting process is carried out in a rotary kiln; the retention time is up to 10 hours.

Reagents could be used for the roasting purpose.

Reagents	Chemical reactions	Temperature
NaCl, vapor	**$2NaCl+H_2O[g] + V_2O_5 \rightarrow 2NaVO_3 + 2HCl\ [g]$**	800-900 °C
NaCl, without vapor	**$2NaCl + V_2O_5 \rightarrow 2NaVO_3 + Cl_2[g]$**	
Soda	**$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2(g)$**	900-1200°C
Na_2SO_4	**$Na_2SO_4 + V_2O_5 \rightarrow 2NaVO_3 + SO_3(g)$**	1200-1230°C

The advantages and disadvantages of these processes are:

Salt roasting	Cheapest, selective attack on vanadium
Soda roasting	Non-selective
Sulfate roasting	Selective, higher temperature

Soda roasting is probably the most used method today due to the high environmental requirement. Common problems for these processes are side reactions.

Free time: formation of insoluble vanadates, therefore should be stabilized by sulfation:

$$\mathbf{2CaO + 3V_2O_5 + 2SO_2 + O_2(g) \rightarrow 2CaSO_4 + 6V_2O_5}$$

2.4.2 Leaching and Solution Purification

Water is the most commonly used leaching reagent but acid and alkali leaching are also used in some applications. Acid leaching with sulfuric acid ensure that insoluble compounds such as calcium, magnesium and iron vanadates will be solved. Alkali leaching with soda can be used to recover uranium and vanadium ores. Solution purification is not always necessary but has been used. Although techniques such as precipitation and ion exchange have been used to achieve this separation, it is only solvent extraction which has been extensively investigated and applied.

The purpose of leaching step is to dissolve vanadium in aqueous solution salt roasted materials in water, acid or alkali solutions. Water is the most common used industrial methods with solution of 30-50 g V_2O_5/l and pH of 7-8 acid (most commonly used H_2SO_4) is used to ensure the water insoluble compounds such as Ca, Mg and Fe vanadates that will dissolved. Alkali/soda where $NaCO_3$ will release V_2O_5 from CaO vanadate. U-V ore where both U and V will be extracted into the aqueous solution 70-80% V and 75-85% U recovered.

$$\mathbf{2CaO\ 3V_2O_5 + 2Na_2CO_3\ (aq) \rightarrow 2CaCO_3 + 3NaVO_3\ (aq)}$$

There are also methods for leaching V from ores, these methods which hardly exist due to environmental reasons, will generate a huge amount of leaching residues. Acid (H_2SO_4) and alkali are also used where as acid used V-sources: U-V ore, catalyst, flay ash, boiler residue, and effective but not selective to vanadium, i.e. impure V-bearing solution will be obtained. As alkali used V-sources are fly ash, boiler residue this method is not as effective as acid but selective to vanadium higher temperature and pressure.

2.4.3 Vanadium Precipitation and V_2O_5 Fusion

Vanadium precipitation is the final operation of the vanadium extraction process. It is important that the vanadium bearing solution is freed from impurities especially phosphorus since vanadium is mainly utilized in the steel industry. The precipitation is determined by pH, concentration and temperature and can be made in many different ways.

V_2O_5 precipitation from boiling solution by acidification with sulfuric acid. The solution is filtered and washed; the red-brown flocculent material is known as “red cake”. The red cake can be further treated in many ways. Drying with air or fusion transforms the red cake to products know as technical grade oxide and fused black oxide respectively.

Vanadium recovery process in red cake is by ammonium metavanadate crystallization (AMC), producing a product containing 99.9% V_2O_5. The leaching of oil-fired fly ash in 0.5N of sulfuric acid lead to an extraction of 75% vanadium. When leached in 2N sodium hydroxide solution the extraction was 80% and when leached with 4N ammonia water the extraction of vanadium was less than the obtainable from leaching in sulfuric acid solution or sodium hydroxide solution [Mefos, 2006].

Vanadium extractions from the major V-bearing raw materials are shown in Figure 2.10.

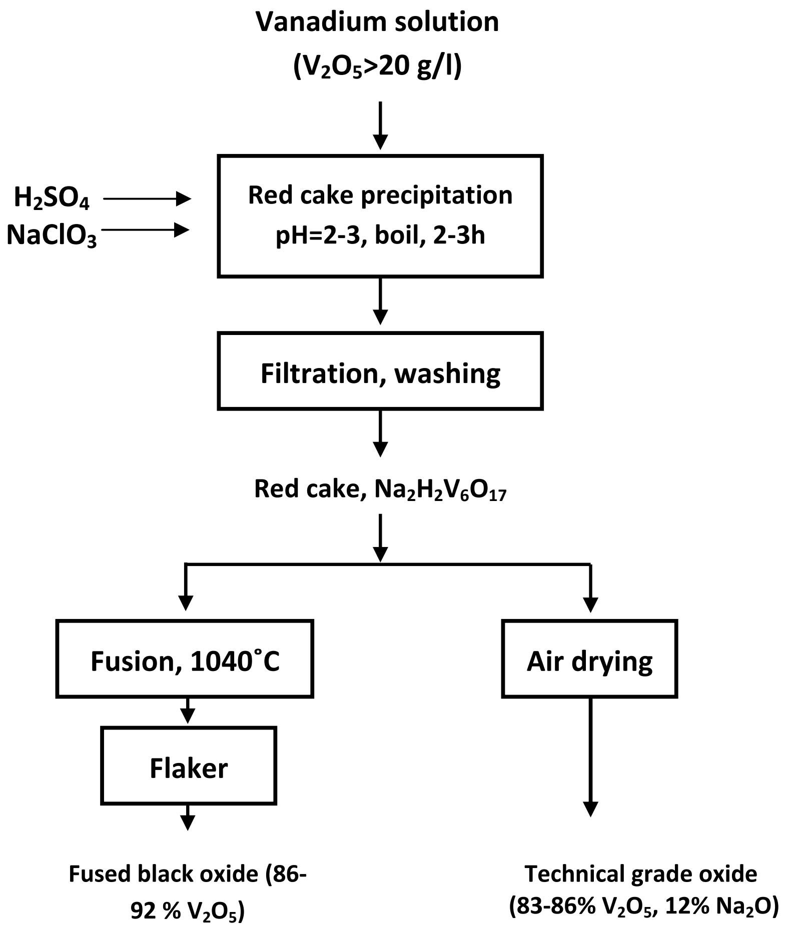

Fig. 2.10 Red cake Precipitation [Mefos, 2006]

Jassim [1998] used a solvent extraction technique as a separation method to separate vanadium from the leach solution of the ashes of burned fuel oil at electrical power station in Iraq. Tributylphosphat (TBP) was used as an extraction agents through mixer-settler batteries. Some parameters, which influences vanadium extraction were studied in detail, such as chloride into concentration and the acidity of the mother solution, in addition to the number of extraction stripping stage and phase ratio; the following conclusion were drawn:

- The percent of 86% extraction of vanadium metal ions from the mother solution was achieved using four stages.
- A quantitive stripping of vanadium metal ions from organic phase TBP was attained using four stages.
- Vanadium of purity more than 99% from accompanied metals was achieved.

2.5 Recovery of Vanadium by Amines Solvent Extraction

In 1966 it was reported that there were eleven solvent extraction plants in the USA for the recovery of vanadium using either tertiary amines or quaternary amines [House, 1967]. Following are brief description of typical plants using amines or alkyl phosphates.

The Edgemont Plant of Mines Development, in South Dakota recovers vanadium from their resin-in-pulp slim tailings. Tailing from past operation, and also from the petroleum ash using sulfuric acid as leaching solution [Rosenbum, 1971].

Extraction in mixer settlers are used to contact the feed solution with a solvent mixture containing 6% D2EHPA (di-(2-ethyl hexa) phosphoric acid) and 3% TBP (tri-n-butyl phosphate) in kerosene. The pH is controlled at 1.9 with ammonia. Vanadium is stripped in four stages using a solution of 140 g H_2SO_4/l at a temperature of 40-52°C.

The strip solution containing 55-65g V_2B_5/L. to prevent a bulb-up of uranium, iron, and molybdenum, a 10% bleed of the stripped solvent is scrubbed with 12% sodium carbonate solution in two stages of mixer settlers. This scrub solution is returned to the uranium stripping circuit for recovery of values. The vanadium is precipitated from the vanadium strip solution as a red cake, and converted to 98% V_2O_5 by heating [Merrit, 1971].

The few sheet for the plant is shown in Figure 2.11.

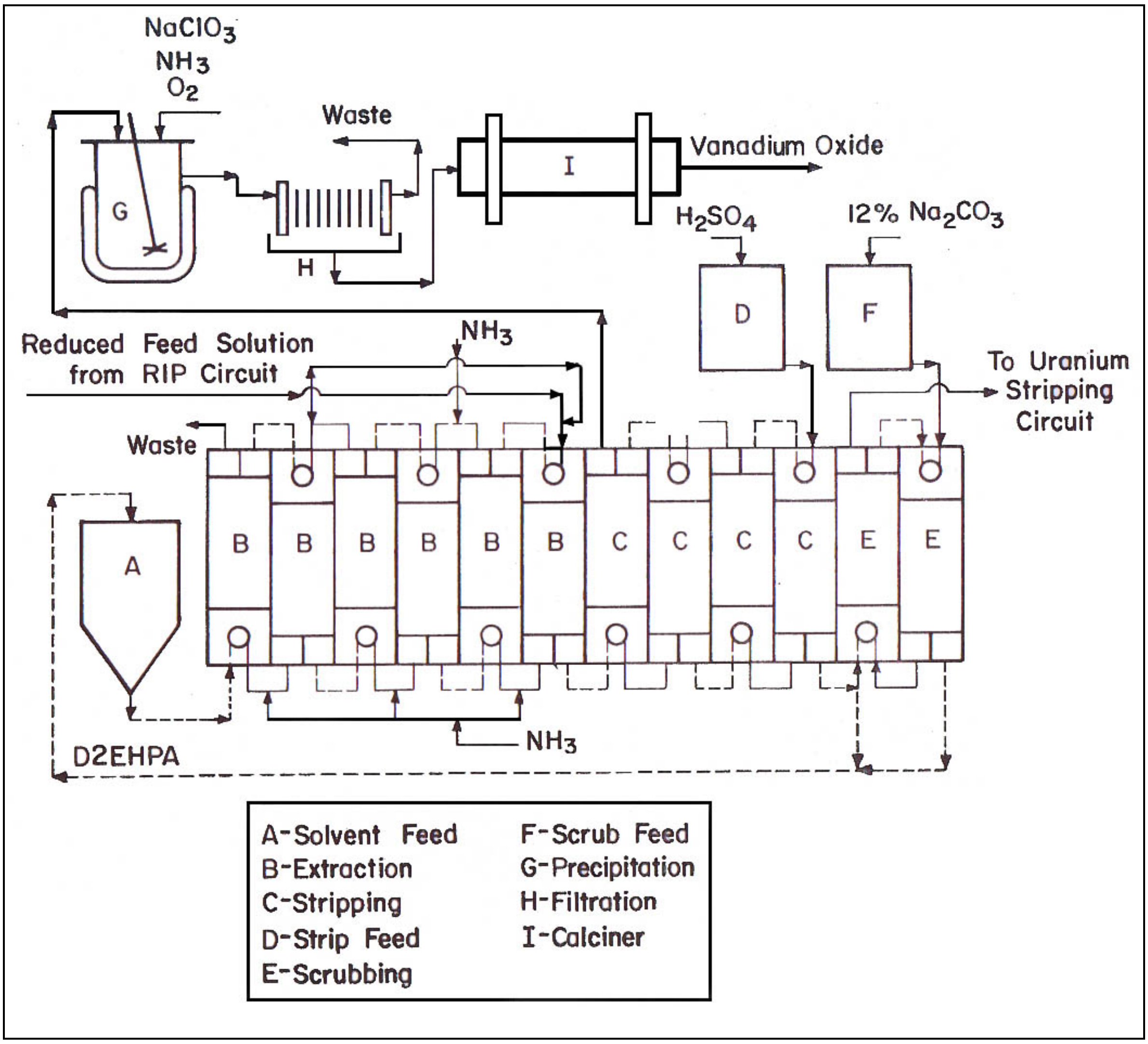

Fig. 2.11 Edgemont plant of mines development for vanadium recovery [Rosenbum, 1971]

At the Union Carbide Plant, Rifle, Colorado, vanadium is recovered using tertiary amines. Following grinding and palletizing, the uranium-vanadium ores are salt roasted in rotary kiln and water leaching. After liquid-solid separation the solution is adjusted to pH 3 with H_2SO_4. Three stages of mixture settler are used for the extraction [Rosenbum, 1971].

Soda ash is used to strip the vanadium followed by precipitation of ammonia metavanadte by addition of ammonia. The water-leached residue is leached with sulfuric acid to dissolve an additional 15% vanadium and uranium.

Uranium is extracted with D2EHPA, and vanadium is precipitated from the raffinate by ammonia. This impure precipitate is recycled to the salt roast stage.

A plant similar in some aspects in the Union Carbide plant at Wilson Springs, Ark. Where the feed solution is again derived from salt roasting and water leaching. Extraction of pentavalent vanadium is at pH 3 with a tertiary amine.

The U.S. Bureau of Mines has been shown the traction of vanadium resulting from sulfuric acid leaching of dolomitic shale.

A 0.075 molar ditridecylamine in kerosene was the preferred extractant as a result of evaluation of secondary tertiary and quaternary amines. Better than 99% of the vanadium was extracted a liquor containing 3g V_2O_5/l at pH 2.5, using three mixer settlers at an aqueous to organic phase ratio of 4, 2 minute mixing per stage was sufficient to load the solvent to 12 V_2O_5/l [Brook et al., 1971].

Vanadium is recovered by stripping with 1.5 molar sodium carbonate solution in two stages of mixer settlers, at an organic to aqueous phase ratio of 8. The resultant solution is precipitated as ammonium metavanadate with ammonia.

Vanadium corporation of America, Durango, Colorado, operated with a mixed solven system, consisting of a mixture of 4.5% tertiary amine, 1.7% D2EHPA, 1.4% heptadecyl phosphoric acid, and 1.3% primary decyl alcohol in kerosene [Merritt, 1971].

The aqueous feed solution, adjusted to pH 1.7 with Na_2CO_3, resulted from the water leach of a salt-roast product. The solution was oxidized with potassium permanganate before extraction. The result of the mixed extractant was a synergistic improvement in extraction. The uranium and vanadium recovered from the solvent by stripping with 10% Na_2CO_3. Any zinc present in the feed was extracted and removed from the solvent by scrubbing with a solution consisting of 5.5% H_2SO_4 and 3% NaCl.

A benzophenoxime was used for the extraction of vanadium V^{+5} form sulfuric acid solutions at pH 0.5 [Agers, 1968].

The vanadium is recovered form the solvent by stripping with an alkaline solution such as an ammonia-ammonium carbonate solution. The extraction of tetravalent vanadium using hydroxamic acid [Wansa, 1959].

Extraction was at a feed pH of 1.0. Vanadium was recovered from the loaded solvent by oxidation and stripping with 0.23 molar NaO_2. The use of a liquate 336, a quaternary ammonium chloride compound, has been described for the recovery of vanadium [Lucas and Ritcey, 1977].

Maximum extraction occurred at pH of 5.1 to 9.3. The stripping time was 1 minute, at room temperature and at an organic to aqueous phase ratio of 5. The extraction equilibrium curve at pH 9.3 is shown in Figure 2.12

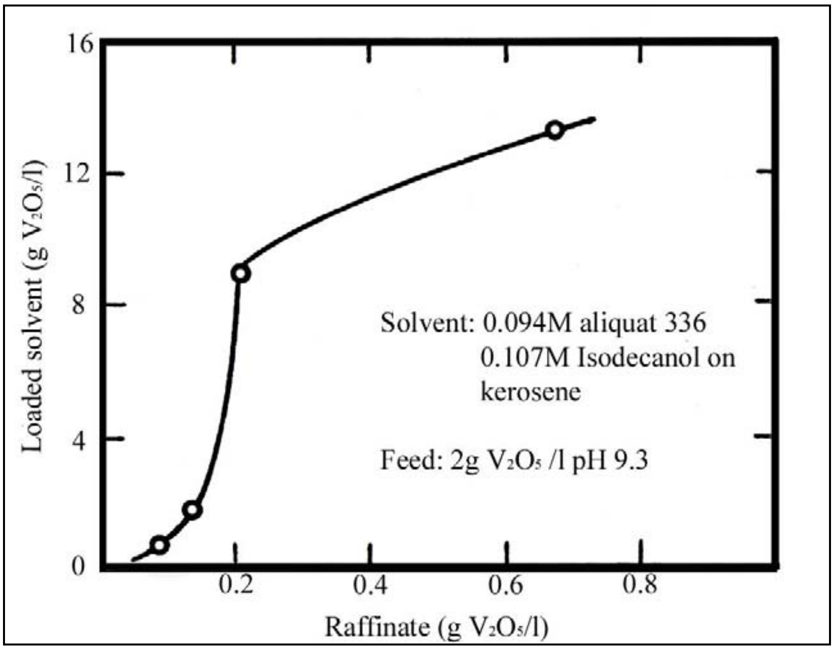

Fig. 2.12 The extraction equilibrium curve

The results of single stage stripping of solvent containing 4.64g V_2O_5/l are shown in Table 2.3.

Chloro complexes of vanadium can be extracted by TBP in CCl_4^- Tedesco and De Rumi [1980]. The extraction of vanadium from HCl solution into pure and CCl_4 solution of TBP has been studied as a fraction of acid and TBP concentrations. Results suggested that vanadium is extracted as a cationic complex by independent mechanism of the extraction of HCl and H_2O. It is shown that below 5M of HCl vanadium extraction is very poor and considering that at 6M of HCl the reduction of vanadium is not very important and is partially constant through 24 hours.

The distribution of vanadium (IV) between hydrochloric acid solution and organic solution of tri-n-octylamine or tricapryl methyl ammonium chloride has been investigated under different conditions. Both phases have been examined, equal volumes 15 ml of phases were shaken for 10 minutes in 50 ml stopper conical flasks in a thermo stated water bath. The mixture was centrifuged, separated and phases were analyzed to give the distribution coefficient. Vanadium was stripped from the organic phase with 1M nitric acid for analysis and determined by back titration [Sato et al., 1974].

Rigg and Garner [1967] showed that VO^{+2} cations can be extracted from chloride solutions containing 0.01-1.0 mol/dm^3 acid by D2EHPA in kerosene.

Table 2.3 The results of single study stripping of solvent [Lucas and Ritcey, 1977]

Stripping reagent	Stripped organic V_2O_5 Analysis [grams / liter]	Per cent V_2O_5 Stripped
2.0M Na_2SO_4	4.60	0.9
1.5M NH_3	4.58	1.31
1.0M Na_2CO_3	3.94	15.1
1.5M NaCl	3.79	18.4
1.0M NaOH	3.60	22.4
1.5M NH_4Cl	2.88	37.8
1.0M NaOH-0.7M Na_2SO_4	2.24	51.8
1.5M NH_4Cl-1.5M NH_3	1.16	75.0
1.5M NaCl-0.75M NaOH	1.10	76.3
1.0M NaOH	0.84	81.8
1.5M NH_4NO_3	0.05	99.0
SO_2	0.0	100.0

Extraction has been found to take place principally through the formation of neutral mononuclear vanadyl complexes with mono-ionized dimmers of hexyldiphosphoric acid (HDPA). At very high solvent loading, it appears that the extracted complex involves HDPA monomer rather than dimer. Most effective extraction is obtained when the diluent has little or no propensity for forming hydrogen bonds with HDPA.

It has been shown that VO^{+2} cation can e extracted from sulfate. The partition of vanadium (IV) between sulfuric acid solutions and solutions of D2EHPA in kerosene has been investigated under different conditions. Both the aqueous and organic phases have been studied by Florence and Fran [1969]. The effect of organic solvent and the addition of TBP on this extraction system have been examined.

2.6 Liquid-Solid Extraction [Rickles, 1965]

Liquid-solid extraction is one of the common mass transfer processes industrially in use. It may be considered as the dissolving of one or more components in a solid matrix by simple solution or by the formation of a soluble form by chemical reaction. The process is one of man's oldest, dating to earliest industrial efforts.

Today, the largest use of liquid-solid extraction techniques is in the extractive metallurgical, vegetable and sugar industries.

The entire field of liquid-solid extraction may be subdivided in a number of ways as in the following fashion:

2.6.1 Leaching

Contacting of a liquid and a solid (usually an ore) and imposing chemical reaction upon one or more substances in the solid matrix so as to render them soluble.

2.6.2 Chemical Extraction

This is simulating to leaching but it applies to removing substances from solid other than ores. The recovering of gelatin from animal bones in the presence of alkali is typical.

2.6.3 Washing Extraction

The solid is crushed to break the cell walls, permitting the valuable soluble product to be washed from the solid matrix. Sugar recovery from cane is a prime example.

2.6.4 Diffusion Extraction

The soluble product diffuses across the denatured cell walls (no crushing involved) and is washed out of the solid. The recovery of beet sugar is an excellent case in point.

There are also several related processes, such as reverse extraction and single-component leaching; reveres extraction involves the adsorption of one or more soluble substances onto a solid surface. Single-component leaching is the dissolving of a pure or relatively pure solid, phases in order to obtain some what higher purity of different crystal habit.

2.7 Methods of Leaching [Rickles, 1965]

The method chosen for leaching an ore will depend mainly upon the value of the metal content of the material, the cost of mining and of bringing the ore to the surface, the cost of any milling and other preleaching treatment such as roasting or melting, and the case of dissolution.

2.7.1 Agitation Leaching

Agitation leaching is carried out on finely ore, it provides mostly high rates of diffusion-layer thickness and rapid dissolution can result. High-temperature pressure leaching is agitation leaching carried out in autoclave and is the most expensive of the leaching methods because of both high capital costs and high operating costs. Agitation leaching at normal atmospheric pressure is extensively used. The reaction vessels are equipped with mechanical impellers. Agitation leaching may be carried out as a batch process or as steady state continuous-flow process. When the leaching has been completed, separation of the solution from the insoluble material is generally necessary.

2.7.2 Precipitation or Vat Leaching

Percolation leaching is applies to related low-grade ores of course particle size 9-12.5 mm. The ore is treated in large vats or tans, which are often fitted with filter-type bottoms to facilitate solution flow through the ore bed. The vats are usually of concrete lined with lead or mastic. Vat capacities vary but may be up to 10,000m3 with the depth generally not greater than 6m. The larger vats may accommodate up to 12,000 tones of ore and filled and emptied mechanically. Either downward or upward percolation may be used but upward flow avoids reduced flow rates caused by blinding of the filter bottoms. Batch leaching is often-practiced for small-scale processing but semi-continuous counter-current leaching, utilizing a sequence of vats, is generally used for large scale conditions.

In the latter case at least one vat is out of the circuit at any one time whilst spent ore is removed and is replaced by fresh ore. At the same time leaching is still producing in the other tanks. Loading and unloading may each take up to 15 hours and the leaching period for a vat load of ore may be of order of one week. This method has the advantage that not requiring expensive filtration plant and is capable of yielding more concentrated pregnant solution when counter-current flow is employed.

2.7.3 In-Situ Leaching or Solution Mining

These are alternative terms for the in place leaching of mineral deposits within the earth's crust without prior removal. It is a technique that has been long used for the recovery of evaporated deposits. In more recent years it has been applied to the extraction of metals from low-grade ores remaining within worked-out mines, and to the recovery of metals directly from ore bodies within the ground.

2.8 Factors Influencing the Rate of Extraction

The solution for the equipment of an extraction process will be influenced by the factors, which are responsible for limiting the extraction rate. Thus, if the diffusion of the solute through the porous structure of residual solids is the controlling factor, the material should be of small size so that the distance the solute has to travel in small. On the other hand if diffusion of the solute from the surface of the particles to the bulk of the solution is sufficiently slow to control the process, high degree of agitation of the fluid is called fro. There are many important factors to be considered as follows:

2.8.1 Particle Size

The particle size influences the extraction in number of way. The smaller size, is the greater interfacial area between the solid and liquid and therefore is the higher rate of transfer of material; further the smaller distance that the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particle from the liquid and drainage of the solid residue are made more difficult. It is generally desirable that the particle size should be small, so that each particle requires approximately the same time of extraction. In particular the production of a large amount of fine material should be avoided as it may wedge in the interstices of the large particles, and impede the flow of the solvent.

For example, copper ore can be leached effectively by sulfuric acid solutions within 4 to 8hrs, if ground to pass through 60-mesh screen, in five days if crushed to 6.5mm granules in 4-6 yeas if 15 mm when the soluble substance is more or less uniformly distributed throughout the solid, or even in solid solution, the leaching action may provide channels for the passage of fresh solvent and fine grinding may not be necessary.

2.8.2 Solvent

The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. Generally a relatively pure solvent will be used initially, but when the extraction proceeds the concentration of solute will increase and the rate of extraction will progressively decrease, first because the concentration gradient will be reduced and secondly because the solution will generally become more viscous.

2.8.3 Temperature

In most cases, the solubility of the material, which is being extracted will increase with temperature to give a higher rate of extraction. Further the diffusion coefficient will be expected to increase within temperature and this will also improve the rate. In some cases, the upper limit of temperature is determined by secondary considerations. Such as the necessity of preventing enzyme action during the extraction of sugar for example.

2.8.4 Agitation

Agitation of the solvent is important because it increases the eddy diffusion and therefore increases the transfer of material from the surface of the particles to the bulk of the solution. Further, agitation of suspensions of fine particles prevents sedimentation and more effective use is made of the interfacial surfaces.

2.8.5 Leaching Time

Leaching time depend greatly on specific conditions of test, i.e. depend on, particle size, solvent, temperature of leaching and agitation.

CHAPTER THREE THEORETICAL WORK

The aim of this works is to explain the previous experimental data of vanadium recovery from South Baghdad Power Station where ash residue (fly ash) was leached with sodium hydroxide solution, determining the controlling step and study the kinetic model to determine the order of reaction and activation energy.

The process variables were temperature, particle size and time of leaching at constant molarity of the sodium hydroxide.

The effects of these variables on the percentage of recovery were investigated by using the experimental design. These variables based on previous work of Mousa [1999].

3.1 Rate Equation for Non-catalytic Heterogeneous Reaction System [Perry and Chilton, 1973 and Smith, 1981]

3.1.1 Mechanism of Un-catalyzed Heterogeneous Reactions

In a heterogeneous reaction system, the overall rate expression becomes complicated because of interaction between physical and chemical processes. This complication is introduced by the requirement that reactants in one phase have to be transported to the other phase containing other reactants where the reactions take place. The physical and chemical rate processes in the non-catalyzed heterogeneous system can he considered to take place in series and/or in parallel. Hence the over all rate expression may be formulated by combining terms for the various process steps involved.

This type of reaction may consist of the following steps:

a. Diffusion of reactants from the bulk of the first phase to the interface between the two phases. If an additional layer of solid product and inert material (e.g., ash in solids) is present at the interface, the reactants would have to overcome the resistance of this layer before they could reach the surface of the second phase, where other reactants are present.

b. Diffusion of reactants from the interface to the bulk of the second phase.
c. Chemical reaction between the reactants from phase one and those in phase two.
d. Diffusion of products within the second phase and/or out of phase two into the bulk of phase one

Whether these four steps proceed successively or simultaneously and which one of the steps controls the overall reaction rate depend upon the phases involved and the specific reaction concerned, as well as on process conditions.

3.1.2 Factors Affecting Heterogeneous Reactions

Since interaction of chemical and physical processes is involved in heterogeneous reactions, the overall rate is under the influence of factors that affect both types of processes. These may include:

a. Mass-transfer factors, e.g., diffusion characteristics of fluid phases.
b. Contact patterns of phases, e.g., each phase may be in one of the two ideal flow patterns, i.e., plug or back-mix flow. There are a number of possible combinations of contacting patterns.
c. Fluid dynamic factors, e.g., mass velocity, degree of turbulence, etc.
d. Interfacial surface area.
e. Geometry of the reaction vessel.

f. Chemical kinetic factors, i.e., activation energy, concentrations of reactants, etc.
g. Temperature and pressure.

Some of these factors are not completely independent and may interact with one another; for example factor (c) would exert influences on factors (a and d) in the case of a fluid-fluid reaction, and it is also related to factors (b and e).

3.2 Reaction Models [Perry and Chilton, 1973, Smith, 1981 and Levenspiel, 1999]

The requirement for a good engineering model is that to be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select model which is very closely reflects reality but which is so complicated that can not do anything with it. Unfortunately, this is all often happens.

Two simple idealized models can be considered, the progressive-conversion model and the unreacted-core model.

3.2.1 Progressive-conversion Model

It can be visualized that the reactant fluid enters and reacts throughout the particles at all times, most likely at different rates at different locations within the particles. Thus solid reactant is converted continuously and progressively throughout the particles as shown in Figure 3.1.

The continuous reaction model may be expected when the reaction is slow with a very porous solid. Here the reaction can occur throughout the solid. Also when the solid is converted by the action of heat, without needing contact with a fluid.

3.2.2 Unreacted-core Shrinking Model

Unreacted-core model deals with the reaction occur first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid. Refer to as "ash." Thus, at any time there exists an unreacted core of material which shrinks in size during reaction, as shown in Figure 3.2.

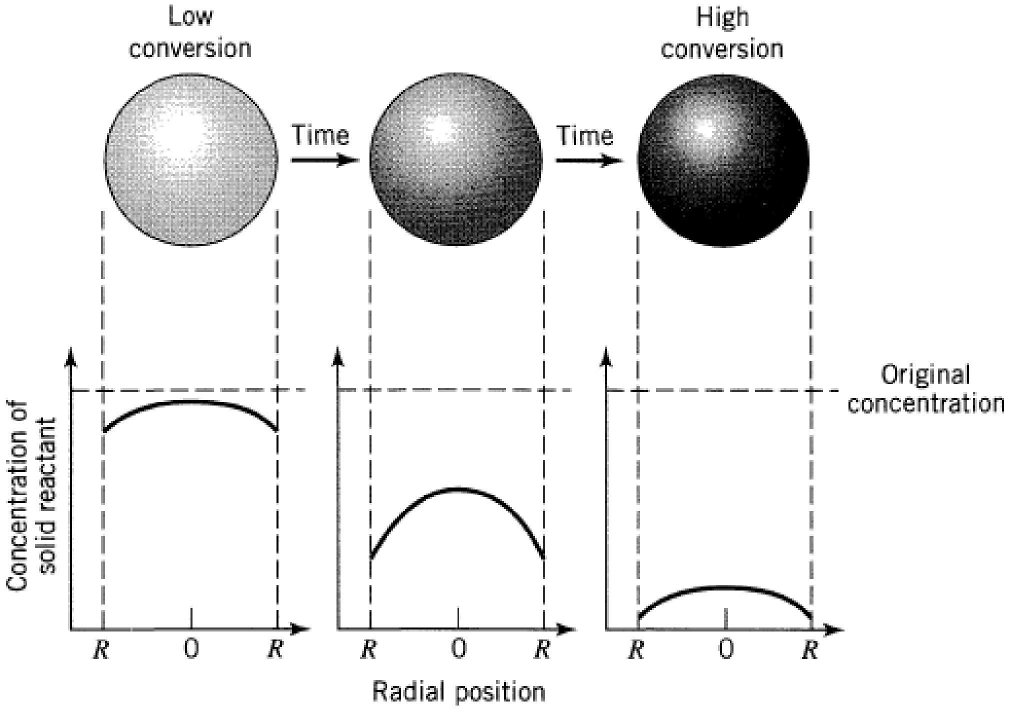

Fig. 3.1 Progressive-conversion model [Levinspiel, 1999]

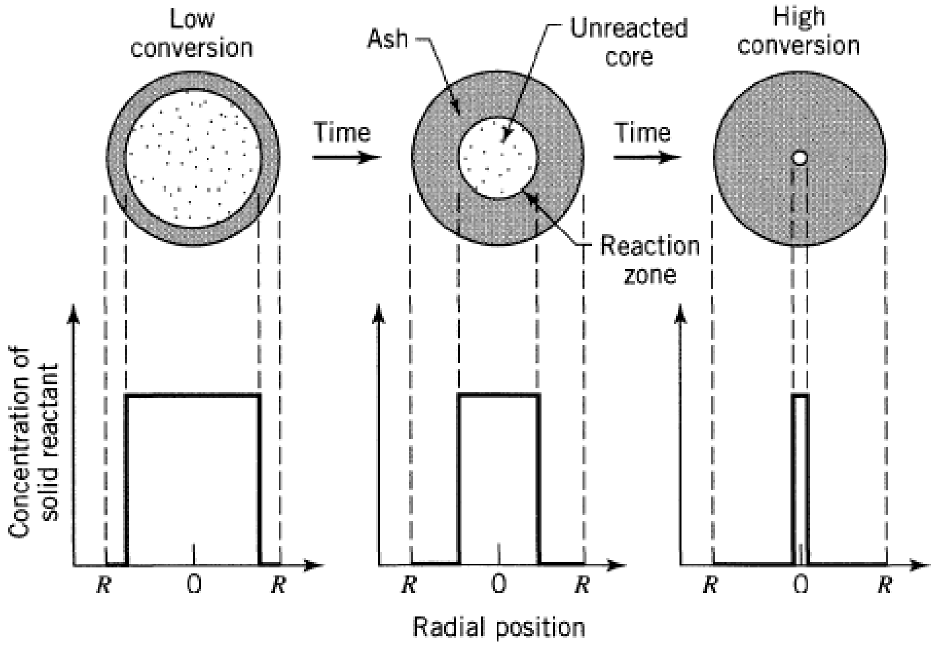

Fig. 3.2 Steps of unreacted-core shrinking model [Levinspiel, 1999]

3.2.3 Unreacted-core Model for Spherical Particles of Unchanged Size

Heterogeneous reaction in which a gas or liquid contacts a solid, reacts with it and transforms it into product, such reaction may be represented by:

$$A(\mathit{fluid}) + b\,B(\mathit{solid}) \rightarrow \mathit{fluid\ and\ solid\ products} \qquad \ldots(3.1)$$

This model was first developed by Yagi and Kunii [1955, 1961], who visualized five steps occurring in succession during reaction (see Figure 3.3).

Step 1. Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.

Step 2. Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.

Step 3. Reaction of gaseous A with solid at this reaction surface.

Step 4. Diffusion of gaseous products through the ash back to the exterior surface of the solid.

Step 5. Diffusion of gaseous products through the gas film back into the main body of fluid.

In heterogeneous reaction there are three resistances that may control the process namely; fluid film, ash layer and chemical reaction, as shown in Figure 3.3.

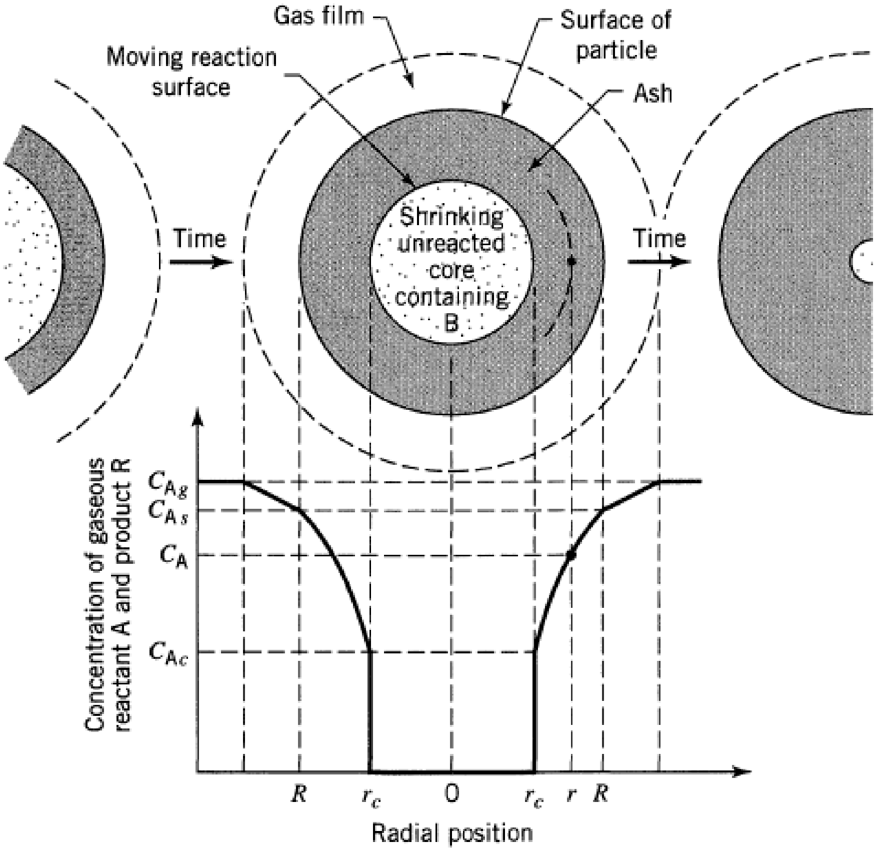

Fig. 3.3 Schematic diagram of concentration profile for the unreacted-core shrinking model [Levinspiel, 1999]

3.2.3.1 Diffusion through Fluid Film Controls

Whenever the resistance of the gas film controls, the concentration profile for gaseous reactant A will be shown as in Figure 3.3. From this figure we see that no gaseous reactant is present at the particle surface; hence, the concentration driving force, C_{Ag} - C_{As}, becomes C_{Ag} and is constant at all times during reaction of the particle.

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt}=-\frac{1}{4\pi R^2}\frac{dN_B}{dt}=-\frac{b}{4\pi R^2}\frac{dN_A}{dt}=bk_g\left(C_{Ag}-C_{As}\right) \quad \ldots(3.2)$$

Where $bk_g\left(C_{Ag}-C_{As}\right)=bk_gC_{Ao}=cons\tan t$

$$N_B=\rho_BV \quad \ldots(3.3)$$

The decrease in volume or radius of unreacted core accompanying the disappearance of dN_B moles of solid reactant or dN_A moles of fluid reactant is then given by:

$$-dN_B=-bdN_A=-\rho_BdV=-\rho_Bd\left(\frac{4}{3}\pi r_c^3\right)=-4\pi\rho_Br_c^2dr_c \quad \ldots(3.4)$$

Replacing Equation 3.4 in 3.2 gives the rate of reaction in term of shrinking radius of unreacted core, or:

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt}=-\frac{\rho_Br_c^2}{R^2}\frac{dr_c}{dt}=bk_gC_{Ao} \quad \ldots(3.5)$$

By integration:

$$t = \frac{\rho_B R}{3bk_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] \qquad \ldots(3.6)$$

From Equation 3.6, at complete reaction;

$$\tau = \frac{\rho_B R}{3bk_g C_{Ag}} \qquad \ldots(3.7)$$

The radius of unreacted core in terms of fractional time for complete conversion is obtained by combining Equations 3.6 and 3.7;

$$\frac{t}{\tau} = 1 - \left(\frac{r_C}{R} \right)^3 \qquad \ldots(3.8)$$

But:

$$1 - X_B = \left(\frac{Volume\, of\ unreacted\ core}{Total\, volume\, of\ \ Particle} \right) = \frac{\left(\frac{4}{3}\right)\pi r_C^3}{\left(\frac{4}{3}\right)\pi R^3} = \left(\frac{r_C}{R} \right)^3 \qquad \ldots(3.9)$$

Therefore;

$$\frac{t}{\tau} = 1 - \left(\frac{r_C}{R} \right)^3 = X_B \qquad \ldots(3.10)$$

3.2.3.2 Diffusion through Ash Layer Controls

The rate of reaction of A through ash layer at any instant is given by its rate of diffusion to the reaction surface, or:

$$-\frac{dN_B}{dt} = 4\pi r^2 Q = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ao} = cons\tan t \qquad \ldots(3.11)$$

But

$$Q_A = \frac{dC_{Ao}}{dr}.De \qquad \ldots(3.12)$$

Combining Equation 3.11 and 3.12 gives;

$$-\frac{dN_B}{dt} = 4\pi r^2 D_e \frac{dC_{Ag}}{dr} = cons\tan t \qquad \ldots(3.13)$$

Integration Equation 3.13 gives;

$$-\frac{dN_B}{dt}\left(\frac{1}{r_c} - \frac{1}{R}\right) = 4\pi D_e C_{Ag} \qquad \ldots(3.14)$$

This expression represents the condition of reacting particle at any time. Eliminating N_A by writing it in terms of r_c as given by Equation 3.4 and replacing in Equation 3.14 gives;

$$t = \frac{\rho_B R^2}{6bD_e C_{Ag}}\left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3\right] \qquad \ldots(3.15)$$

The time required for complete conversion of a particle ($r_c = 0$) is;

$$\tau = \frac{\rho_B R^2}{6bD_e C_{Ag}} \qquad \ldots(3.16)$$

Dividing Equation 3.15 by Equation 3.16 gives;

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \qquad \ldots(3.17)$$

And;

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \qquad \ldots(3.18)$$

3.2.3.3 Chemical Reaction Controls

When chemical reaction controls, the rate of reaction is given by;

$$-\frac{1}{4\pi r_c^2}\frac{dN_B}{dt} = -\frac{b}{4\pi r_c^2}\frac{dN_A}{dt} = bk''C_{Ag} \qquad \ldots(3.19)$$

Writing N_B in term of the shrinking radius, as in equation 3.4 gives;

$$-\frac{1}{4\pi r_c^2}\rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = bk''C_{Ag} \qquad \ldots(3.20)$$

Or;

$$t = \frac{\rho_B}{bk''C_{Ag}}(R - r_c) \qquad \ldots(3.21)$$

The time required for complete conversion is given when r_c equal to zero;

$$\tau = \frac{\rho_B R}{b k'' C_{Ag}} \qquad \text{...(3.22)}$$

Combining Equations 3.21 and 3.22 gives;

$$\frac{t}{\tau} = 1 - \frac{r_C}{R} = 1 - (1 - X_B)^{1/3} \qquad \text{...(3.23)}$$

3.3 Differential Method of Analysis

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative d(concentration) / d(time), and testing the goodness of fit of the equation with experiment.

The procedure is as follows:

1. Plot the concentration versus time data, and then by eye carefully curve will be drawn to represent data. This curve most likely will not pass through all the experimental points.
2. Determine the slop of this curve at suitably selected concentration values. These slops are the rates of reaction rate (r_A) at these compositions.
3. Now search for a rate expression to represent this r_A versus concentration data, either by:
   - Picking and testing a particular rate form: (see Figure 3.4)

$$-r_A = k f(C_A) \qquad \text{...(3.24)}$$

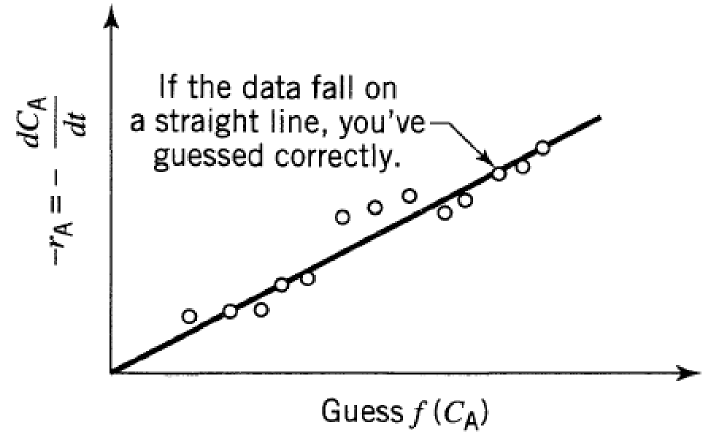

Fig. 3.4 Test for the particular rate (equation 2.37) by the differential method [Levenspiel, 1999]

- Testing an nth-order form the below equation by taking logarithms of the rate equation (see Figure 3.5).

$$-r_A = kC_A^n \qquad \ldots(3.25)$$

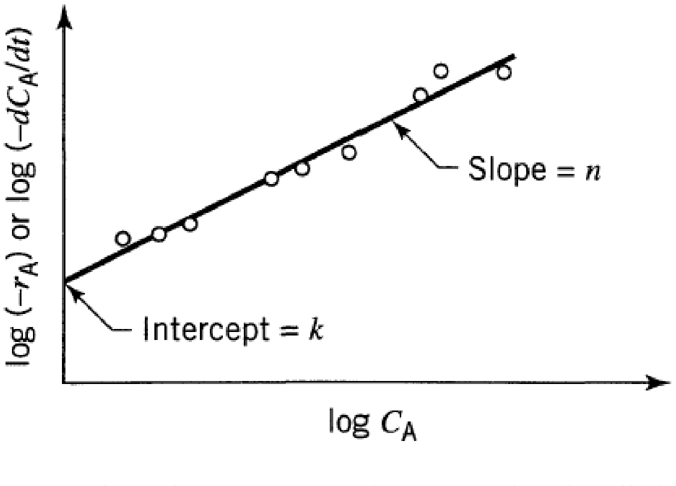

Fig. 3.5 Test for an nth-order rate (equation 2.38) by the differential method [Levenspiel, 1999]

3.4 Temperature-dependent of a Rate Equation

For many reactions, the rate expression can be written as a product of temperature-dependence term and composition-dependence term or

$$r_i = f_1(temperature).f_2(composition) \qquad \ldots(3.26)$$

$$r_i = k.f_2(composition) \qquad \ldots(3.27)$$

For such reactions the temperature-dependence term, the reaction rate coefficient has been found practically in all cases to be well represented by Arrhenius' law:

$$k = A_o \exp\left(\frac{-E}{RT}\right) \qquad \ldots(3.28)$$

Where A_o is called the frequency or pre-exponential factor and E is called the activation energy of the reaction. This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency.

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Figure 3.6 and Table 3.1.

These findings are summarized as follows:

1. From Arrhenius' law a plot of lnk versus 1/T gives a straight line, with slope for large E and small slope for small E.

2. Reactions with high activation energies are very temperature-sensitive; reactions with low activation energies are relatively temperature-insensitive.

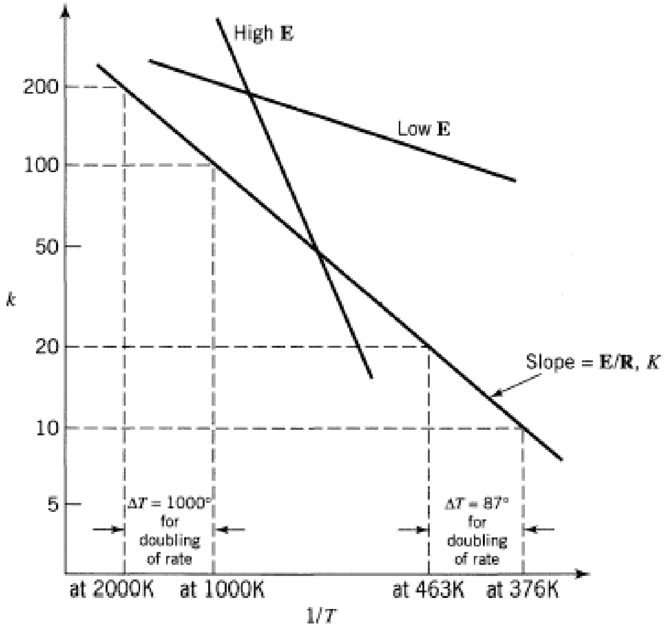

Fig. 3.6 Sketch showing temperature dependency of the reaction rate [Levenspiel, 1999]

Table 3.1, Temperature rise needed to double the rate of reaction for activation energies and average temperatures shown [Levenspiel, 1999]

Average temperature, ^{o} C	Activation Energy, kJ/mol			
	40	160	280	400
0	11	2.7	1.5	1.1
400	65	16	9.3	6.5
1000	233	58	33	23
2000	744	185	106	74

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Mathematical Correlation

A second order polynomial mathematical correlation was employed in the range of the independent variables (temperature (X_1), particle size (X_2) and time (X_3)). The general form of second order polynomial for these variables represented by the following equation:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1^2 + a_5X_2^2 + a_6X_3^2 \\ + a_7X_1X_2 + a_8X_1X_3 + a_9X_2X_3 \qquad \ldots(4.1)$$

Table 4.1 shows the experiments, which were extracted from Mosa [1999]. For postulating the best form of the above equation, the data of Table 4.1 is first fitted with Equation 4.1so that the analysis of variance of central composite design could be applied. By this analysis, each effect of the fitted polynomial equation could be tested for its significance.

The analysis of variance (F-test) is used for testing the significance of each effect in Equation 4.1. Using the data given in Table 4.1, the coefficients in Equation 4.1 can be calculated simply by using least square method.

After the coefficient values of Equation 4.1 calculation, it is possible to compute values of vanadium conversion (Y_i) and the corresponding residual $e_i=Y-Y_i$.

As estimate of the experimental error variance Sr^2 is obtained by dividing the residual sum of square $\sum e_i^2$ by γ (number of degree of freedom).

$$\gamma = No.of\ \text{exp}eriments - No.of\ coefficients\ in\ equation \qquad \ldots(4.2)$$

So: γ=72-10=62. And,

$$S_r^2 = \sum \frac{e_i^2}{\gamma} \qquad \ldots(4.3)$$

The estimated variance of coefficients S_a^2 is then calculated by Equation 4.4.

$$S_a^2 = \frac{S_r^2}{\sum X^2} \qquad \ldots(4.4)$$

The significance of effects may be estimated by comparing the value of the ratio $\frac{a^2}{S_a^2}$ (F-calculated) with the critical value $F_{0.95}(1,62) = 4.00$ (the F-distribution at 95 % of confidence level with 1 and 68 degree of freedom).

The coefficient value (A) is used for estimation of F-calculated ($\frac{a^2}{S_a^2}$) and significance are shown in Table 4.2.

Table 4.1 Experimental data and predicted vanadium conversion

Temperature (X_1), K	Particle size (X_2), µm	Time (X_3), h	Experimental conversion (Y_{exp}), %	Predicted conversion (Y_{pre}), %
333	200	1	19.23	20.94
333	200	2	22.50	22.65
333	200	3	25.00	24.34
333	200	4	27.50	26.01
333	200	5	30.00	27.67
333	200	6	30.63	29.31
333	200	7	30.63	30.94
333	200	8	31.25	32.56
353	200	1	50.00	49.66
353	200	2	51.25	51.18
353	200	3	54.38	52.68
353	200	4	56.25	54.17
353	200	5	57.30	55.65
353	200	6	56.00	57.10
353	200	7	55.38	58.55
353	200	8	55.00	59.98
373	200	1	89.38	85.79
373	200	2	92.5	87.13
373	200	3	93.44	88.44
373	200	4	92.40	89.75
373	200	5	91.80	91.03
373	200	6	91.25	92.31
373	200	7	90.00	93.57
373	200	8	88.75	94.81
333	150	1	45.00	51.56
333	150	2	48.75	53.04

Temperature (X_1), K	Particle size (X_2), µm	Time (X_3), h	Experimental conversion (Y_{exp}), %	Predicted conversion (Y_{pre}), %
333	150	3	51.25	54.50
333	150	4	55.63	55.95
333	150	5	58.13	57.39
333	150	6	60.31	58.81
333	150	7	61.56	60.21
333	150	8	62.50	61.60
353	150	1	60.00	66.35
353	150	2	65.00	67.64
353	150	3	67.50	68.92
353	150	4	70.00	70.18
353	150	5	71.25	71.43
353	150	6	72.50	72.67
353	150	7	72.50	73.89
353	150	8	73.44	75.09
373	150	1	87.5	88.55
373	150	2	89.38	89.66
373	150	3	91.25	90.75
373	150	4	93.44	91.83
373	150	5	94.38	92.89
373	150	6	94.38	93.94
373	150	7	95.00	94.97
373	150	8	93.44	95.99
333	125	1	46.25	50.21
333	125	2	51.25	51.58
333	125	3	53.75	52.93
333	125	4	56.25	54.26
333	125	5	59.68	55.59

Temperature (X_1), K	Particle size (X_2), µm	Time (X_3), h	Experimental conversion (Y_{exp}), %	Predicted conversion (Y_{pre}), %
333	125	6	61.25	56.89
333	125	7	63.75	58.19
333	125	8	64.38	59.46
353	125	1	52.50	58.03
353	125	2	57.19	59.21
353	125	3	61.25	60.38
353	125	4	63.75	61.53
353	125	5	65.00	62.67
353	125	6	65.94	63.79
353	125	7	66.25	64.90
353	125	8	67.03	65.99
373	125	1	71.25	73.27
373	125	2	75.00	74.26
373	125	3	76.25	75.24
373	125	4	77.50	76.21
373	125	5	78.75	77.16
373	125	6	79.10	78.10
373	125	7	77.50	79.02
373	125	8	76.88	79.92

Table 4.2 Calculated values of Equation 4.1 coefficients

Coefficient No.	Effect of	A_i	Std. Error	F-calculated	Significantly
0	-	27.58	6.8400	16.26	S.
1	X_1	-2.98	0.0990	906.07	S.
2	X_2	1.262	0.0646	381.64	S.
3	X_3	10.02	0.4000	627.50	S.
4	X_1^2	0.0117	0.0006	380.25	S.
5	X_2^2	-0.0076	0.0002	1444.00	S.
6	X_3^2	-0.295	0.0237	154.93	S.
7	X_1X_2	0.0147	0.0020	5402.25	S.
8	X_1X_3	-0.045	0.0029	240.79	S.
9	X_2X_3	-0.0148	0.0015	97.39	S.
Correlation Coefficient R = 0.9990, Variance = 0.9981, F(1,62) = 4.00 Confidence level = 95 %					

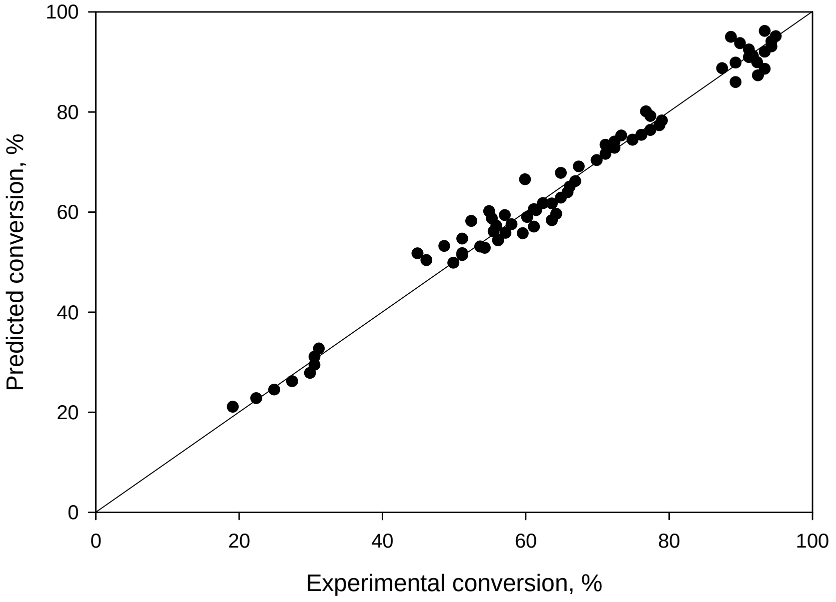

Fig. 4.1 Predicted versus experimental data

4.2 Effect of Different Variables on the Conversion

4.2.1 Effect of Time and Temperature

The effect of time on vanadium conversion at different temperatures and a given particle size is shown in Figures 4.2 to 4.4.

Referring to Figure 4.2, at 200 µm and 373 K, the best conversion was 0.9344 at time of 3 hours. Also, Figure 4.3 shows that at 150 µm and 373 K the time required to achieve conversion of 0.95 was 7 hours, while from Figure 4.4, the best conversion was 0.791 at 125 µm and time of 6 hours.

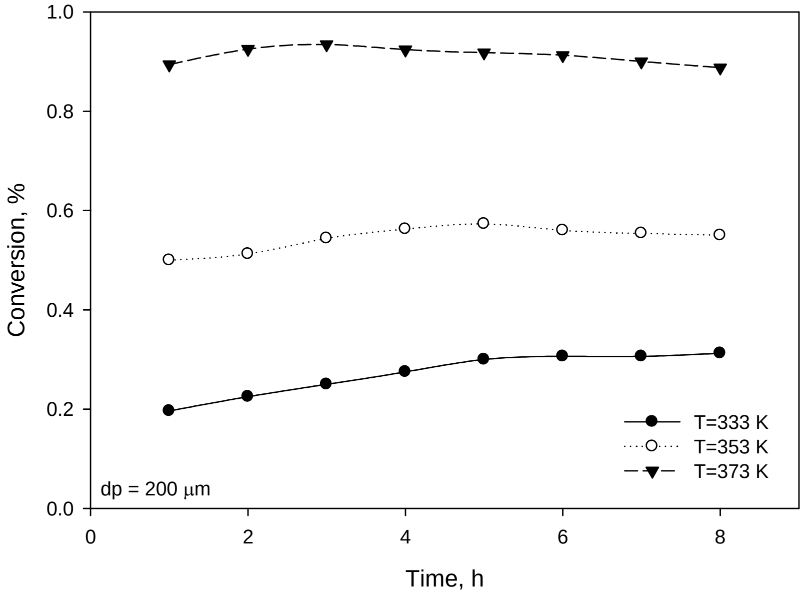

Fig. 4.2 Vanadium conversion versus time at different temperatures and 200µm particle size

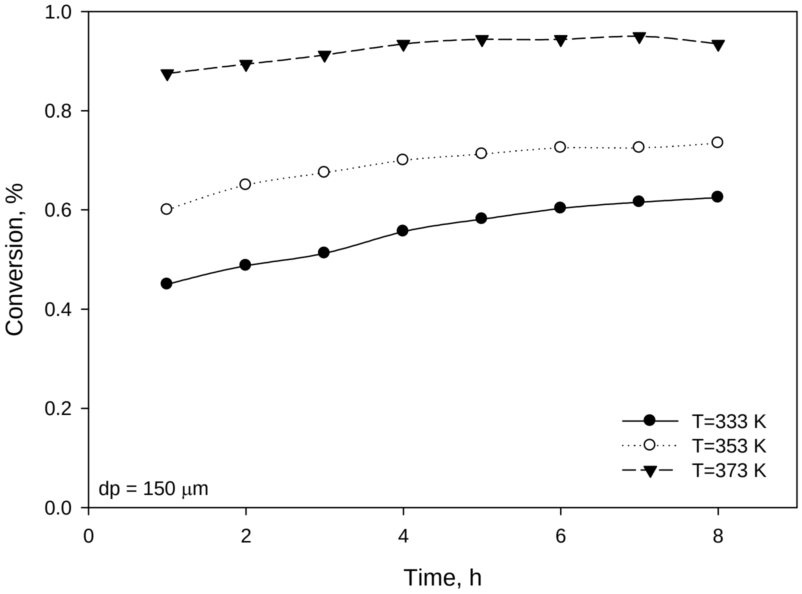

Fig. 4.3 Vanadium conversion versus time at different temperatures and 150μm particle size

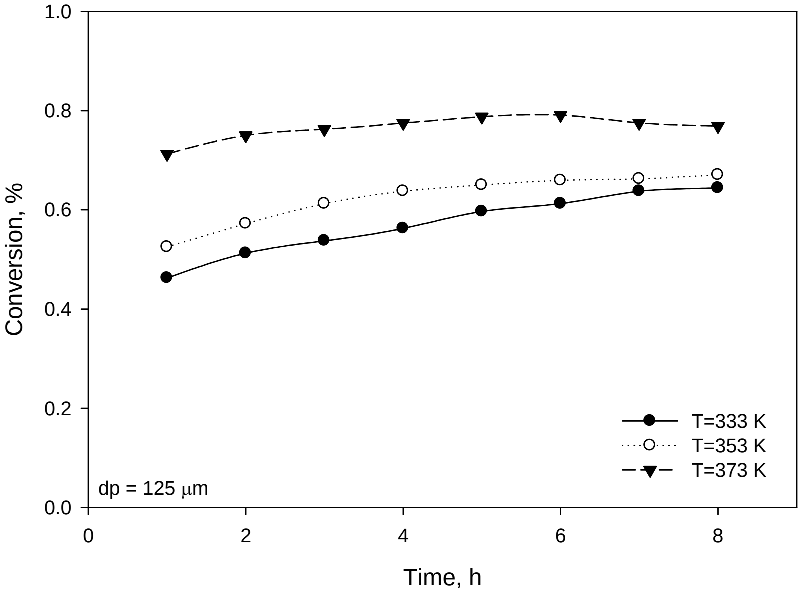

Fig. 4.4 Vanadium conversion versus time at different temperatures and 125μm particle size

From these figures, it can be seen that the vanadium conversion increase as the time increases, also it is obvious that best reaction time which leads to maximum conversion of vanadium is greatly dependent on the specific condition of the test i.e. particle size and temperature of the test.

Figures 4.5 to 4.7 show the effect of time on the conversion at different particle sizes and given temperatures.

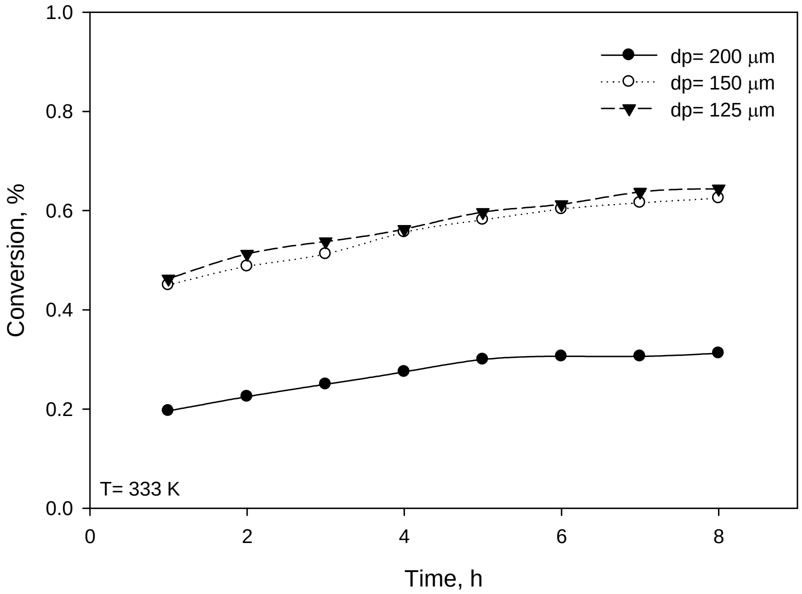

Fig. 4.5 Vanadium conversion versus time at different particle sizes and 333K temperature

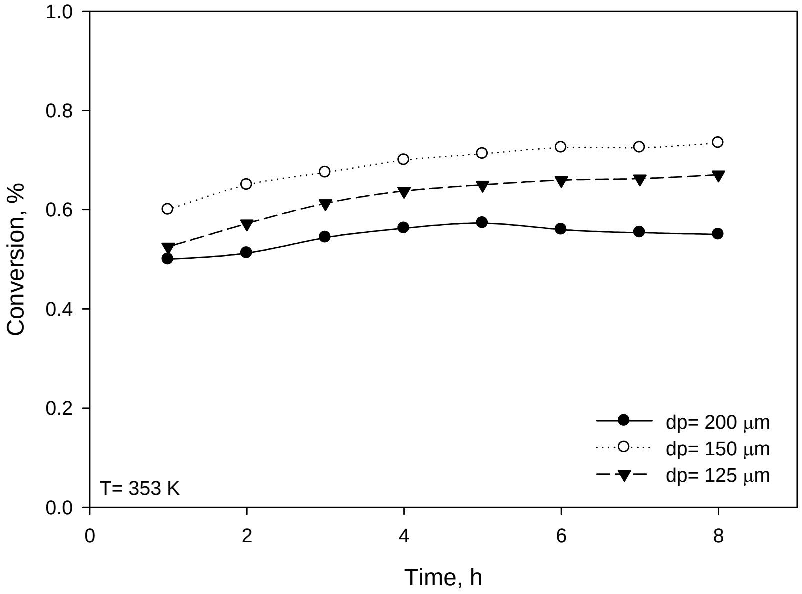

Fig. 4.6 Vanadium conversion versus time at different particle sizes and 353K temperature

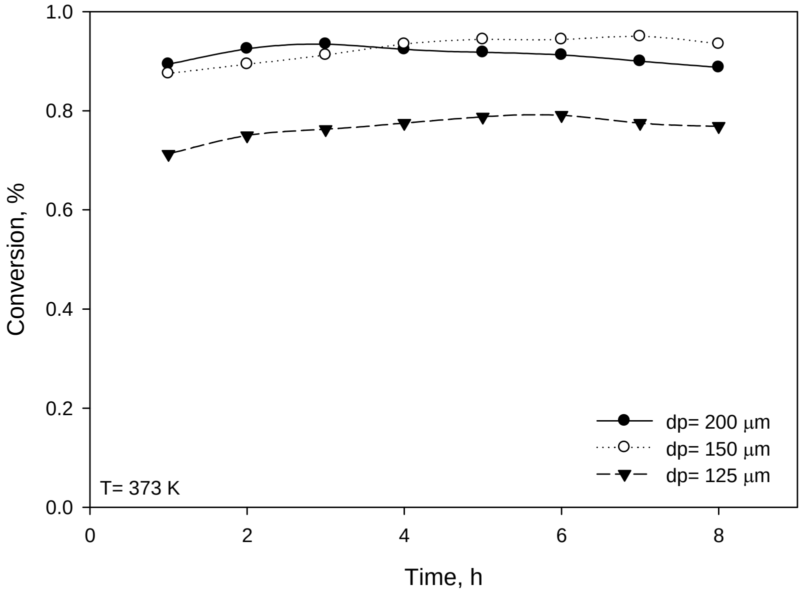

Fig. 4.7 Vanadium conversion versus time at different particle sizes and 373K temperature

Examining these figures, it can be shown that increasing the temperature will increase the conversion. The temperature influences the conversion in number of ways. Firstly as the temperature increases, the mobility of the molecules will increase due to more energy gain. Secondly, the effective diffusivity increases with the increase in the temperature (this is coincided with the definition of the diffusivity). Referring to these figures, which clearly illustrate the interaction between temperature and particle size, the conversion at 333 K and 200 μm is 0.28 increasing to 0.60 for 150 μm at the same temperature.

4.2.2 Effect of Particle Size

The effect of particle size on vanadium conversion at different temperature and a given time is shown in Figures 4.8 to 4.10.

From these figures, it can be seen that the conversion increase as the particle size decrease. The particle size influences the conversion in a number ways. The smaller size is the greater interfacial area between the solid and liquid, the rate of reaction and the rate of transfer of material are higher. A reduction in particle size usually results in a decrease in the average time of passage of solvent from the surface to the interior of the particle and decrease the average time of passage of solute molecules from the dissolving point in the interior of solid particle to the surface of the particle.

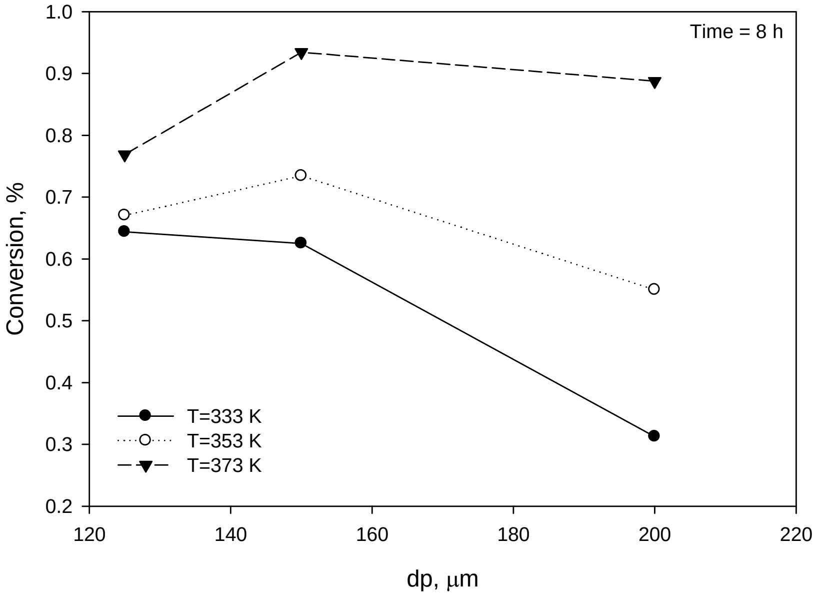

Fig. 4.8 Vanadium conversion versus particle size at different temperatures and 8 h time

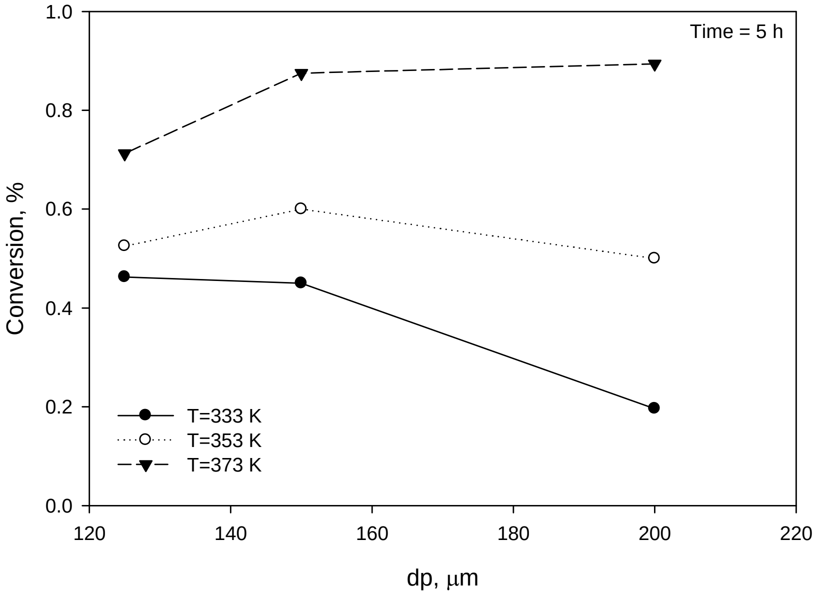

Fig. 4.9 Vanadium conversion versus particle size at different temperatures and 5 h time

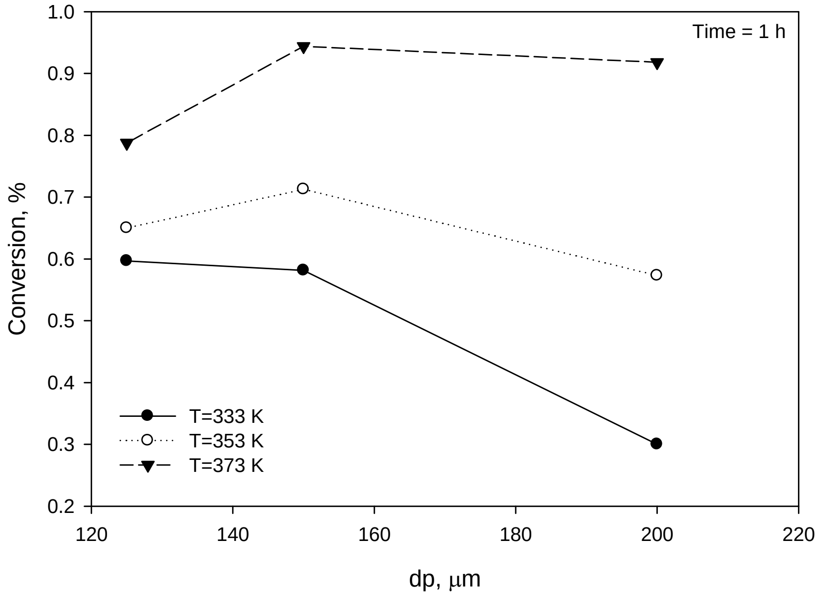

Fig. 4.10 Vanadium conversion versus particle size at different temperatures and 1 h time

The choice of optimum particle size is affected by temperature by referring to the figures, it can be seen that at 60° C the optimum particle size is 125 μm, while at 100° C maximum conversion was obtained at particle size of 150 μm.

4.3 Time for Complete Conversion and Controlling Step

The time for complete conversion was calculated from given data of time and conversion according to constant spherical particle shape of shrinking-core model [Levenspiel, 1999] for constant particle size in heterogeneous in which a gas or liquid contact a solid, reacts and transforms it into product.

For film diffusion controls Equation 3.10 is used

$$\frac{t}{\tau} = X_B \qquad \ldots(3.10)$$

For ash diffusion controls Equation 3.18 is used

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \qquad \ldots(3.18)$$

And for chemical reaction controls Equation 3.23 is used.

$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3} \qquad \ldots(3.23)$$

Where t is time of reaction (h), X_B is conversion of vanadium and τ is time for complete conversion.

Figures 4.11 to 4.19 show the calculation of τ for given temperature and particle size for the shrinking-core model for spherical particles of unchanging size where this model was first developed by Yagi [1955] and Kunii [1961].

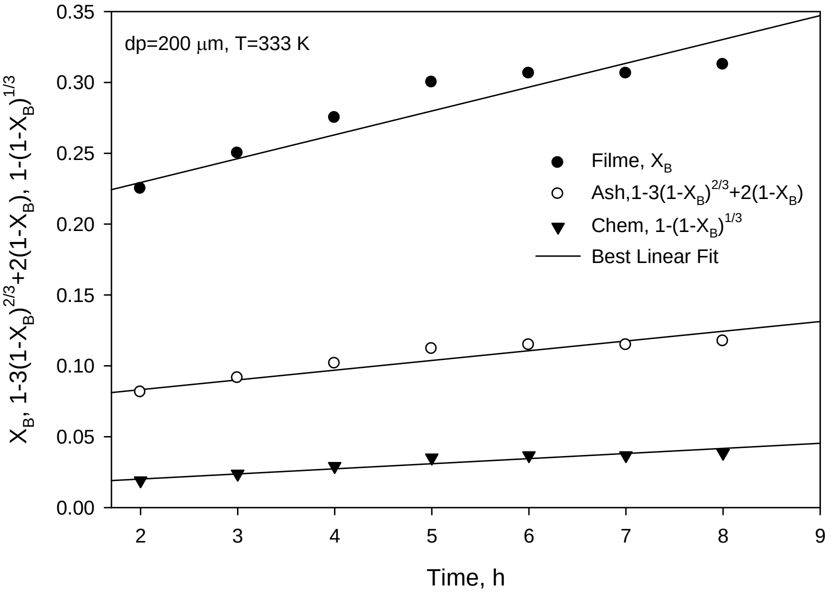

Fig. 4.11 Time constant versus time for various controlling steps at 333 K and particle size of 200 μm

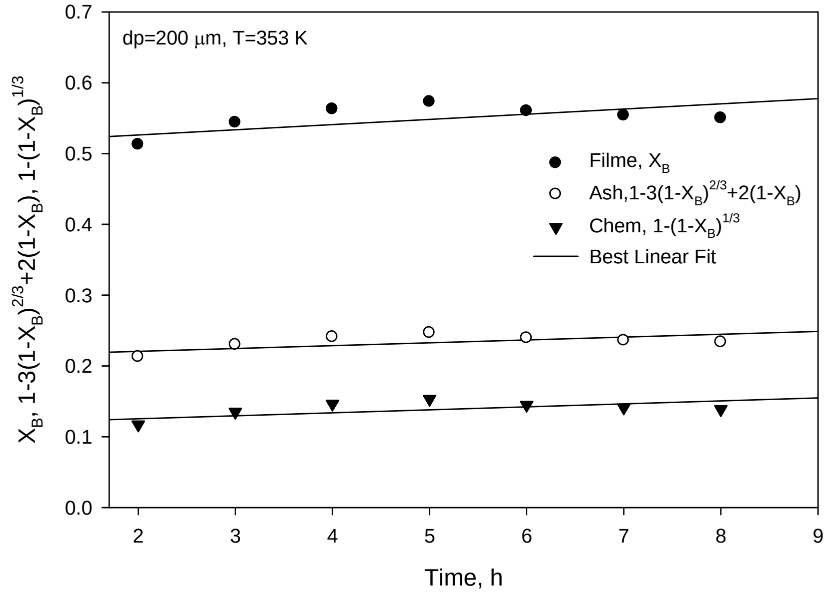

Fig. 4.12 Time constant versus time for various controlling steps at 353 K and particle size of 200 μm

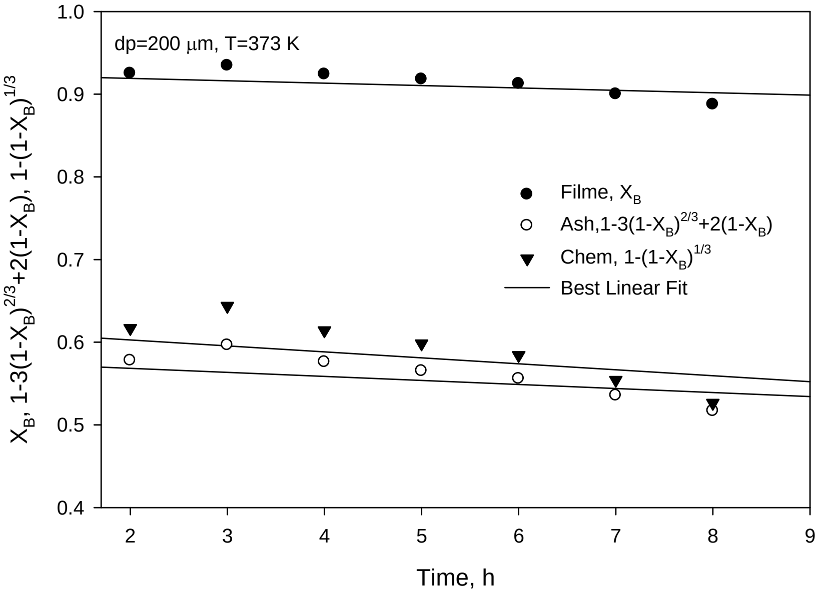

Fig. 4.13 Time constant versus time for various controlling steps at 373 K and particle size of 200 μm

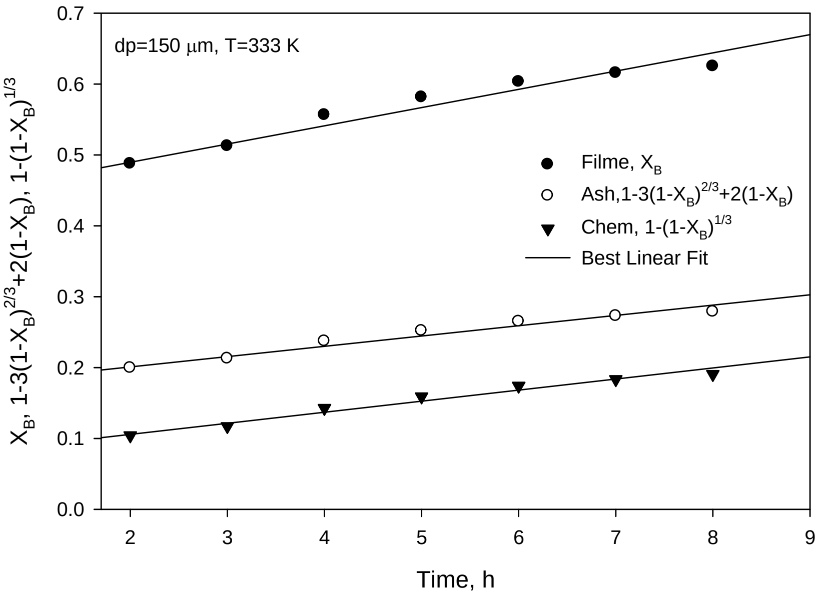

Fig. 4.14 Time constant versus time for various controlling steps at 333 K and particle size of 150 μm

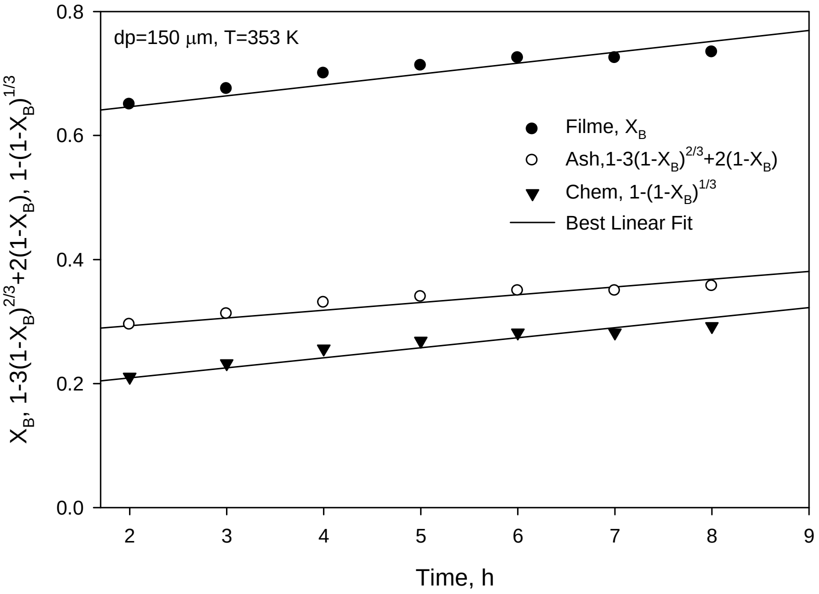

Fig. 4.15 Time constant versus time for various controlling steps at 353 K and particle size of 150 μm

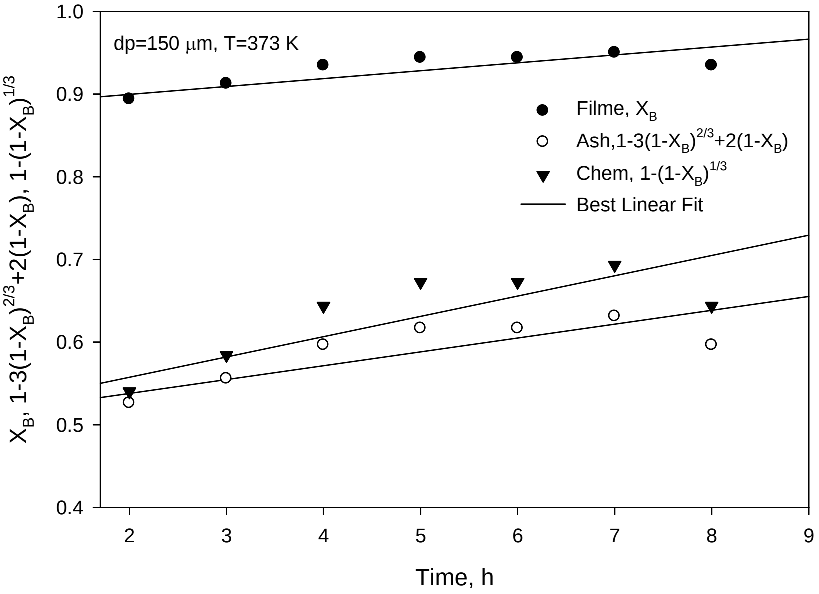

Fig. 4.16 Time constant versus time for various controlling steps at 373 K and particle size of 150 μm

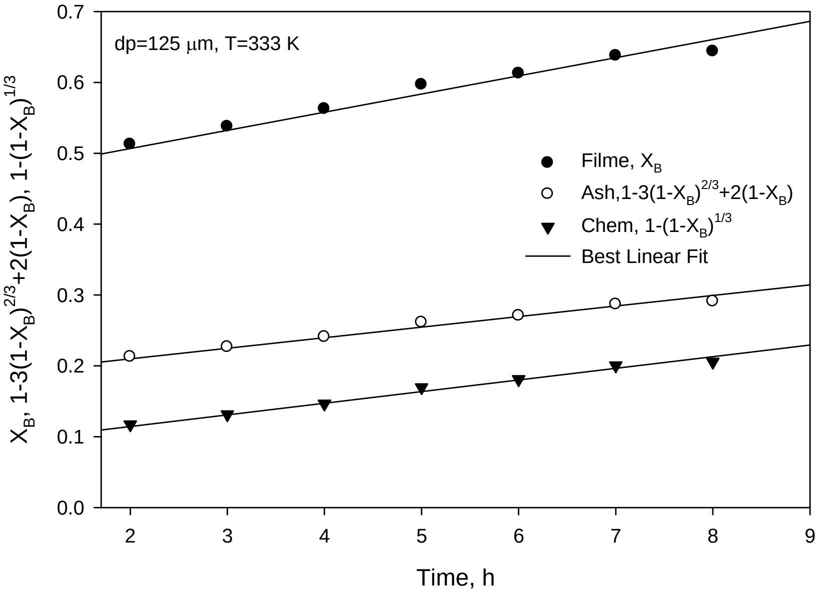

Fig. 4.17 Time constant versus time for various controlling steps at 333 K and particle size of 125 μm

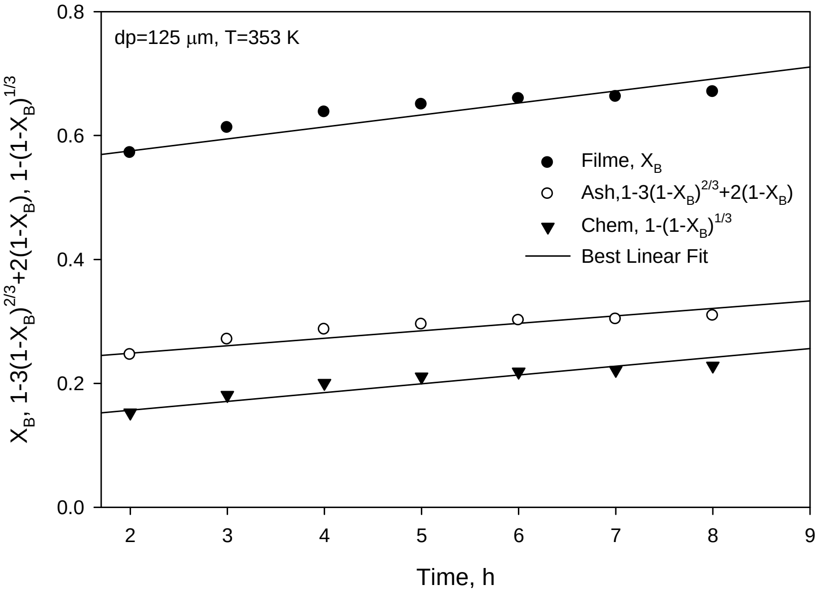

Fig. 4.18 Time constant versus time for various controlling steps at 353 K and particle size of 125 μm

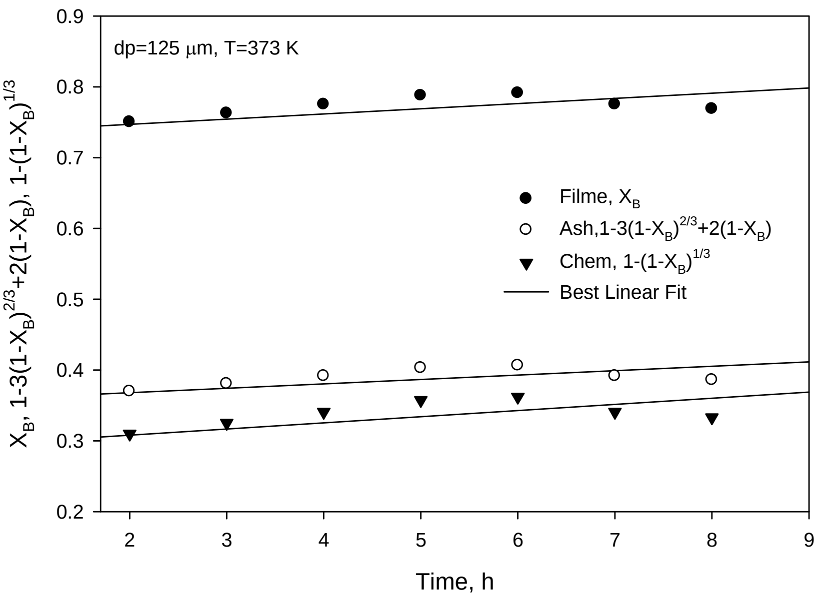

Fig. 4.19 Time constant versus time for various controlling steps at 373 K and particle size of 125 μm

It is obvious from above figures that the time for complete conversion (τ) of the different steps usually vary greatly one from the other. In such cases, it may consider that step with the highest τ to be the rate-controlling step [Levenspiel, 1999].

The rate controlling step of a fluid-solid reaction is deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. This information can be obtained in various ways depending on the facilities available and the materials at hand. The following observations are a guide to experimentation and to the interpretation of experimental data.

The chemical step is usually much more temperature-sensitive than physical steps; hence, experiment at different temperatures should easily distinguish between ash or film diffusion on one hand and chemical reaction on the other as the controlling step.

The kinetics runs with different sizes of particles can distinguish between reaction in which the chemical and physical steps control.

When a hard solid ash forms during reaction, the resistance of gas-phase reactant through this chemical reaction is usually much greater than through the gas film surrounding the particle. Hence, in the presence of non-flaking ash layer, film resistance can safely be ignored. In addition, ash resistance is unaffected by changes in gas velocity.

Thus, as it notice from previous tables, the diffusion through chemical reaction is the controlling step which has the highest resistance among other steps as shown in table 4.3.

Table 4.3 Time constant for different controlling steps

dp, μm	Temp., K	Film time constant, h	Ash time constant, h	Chem. time constant, h
200	333	19.61	52.63	200.00
	353	10.31	24.39	41.67
	373	6.25	9.90	10.31
150	333	9.71	22.73	35.71
	353	8.00	16.95	21.28
	373	6.10	8.77	9.52
125	333	9.43	21.74	33.33
	353	8.77	19.61	27.78
	373	7.35	14.49	16.67

Figures 4.20 to 4.28 show the plot of time versus $\frac{t}{\tau}$ which it is clear to see that the resistance to ash diffusion is the controlling step. Examining Figure 4.27, it can be seen that at temperature of 373 K and particle size of 150 μm, the controlling step will change from ash to chemical reaction resistance where these conditions are the optimum for complete vanadium conversion.

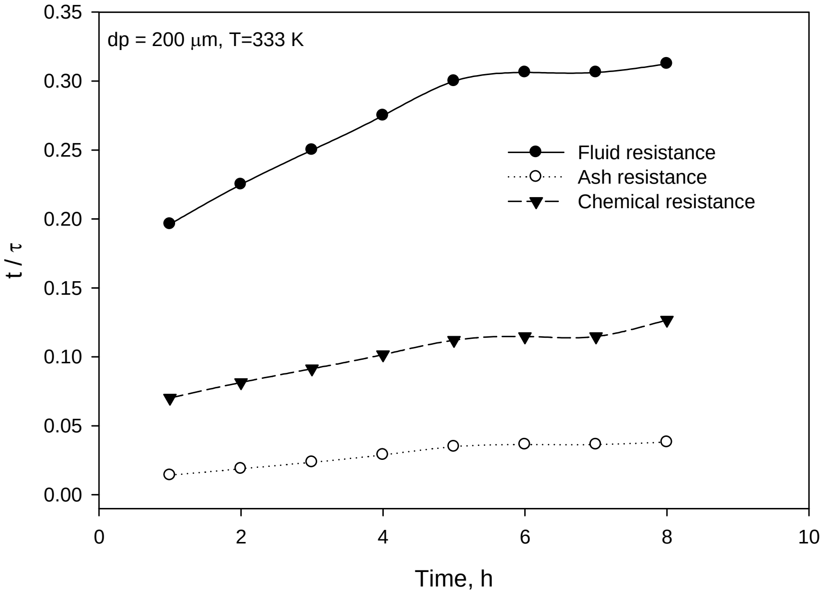

Fig. 4.20 t/τ for fluid, ash and chemical resistance versus time at 200μm particle size and 333 K temperature

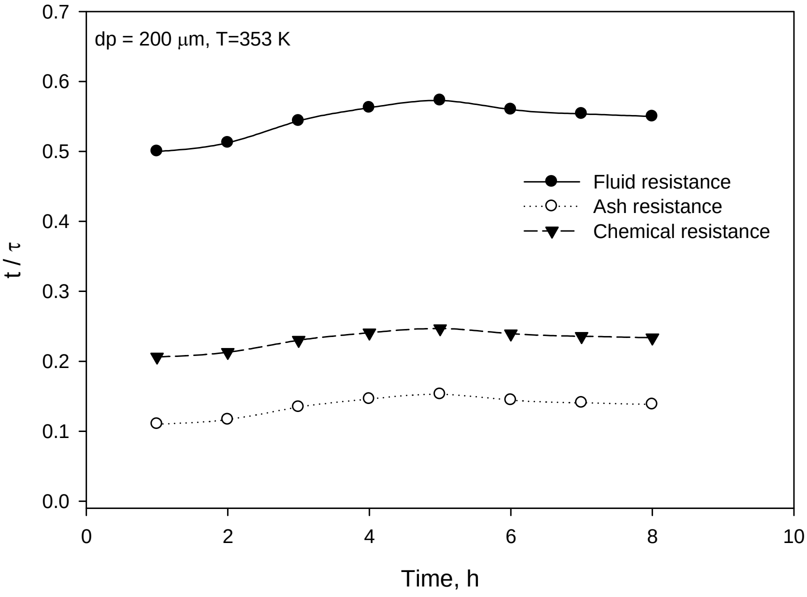

Fig. 4.21 t/τ for fluid, ash and chemical resistance versus time at 200μm particle size and 353 K temperature

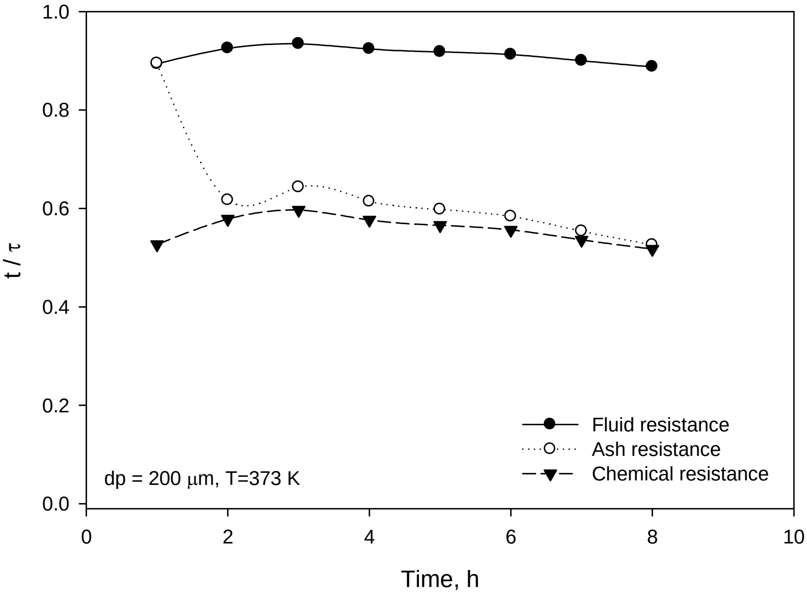

Fig. 4.22 t/τ for fluid, ash and chemical resistance versus time at 200μm particle size and 373 K temperature

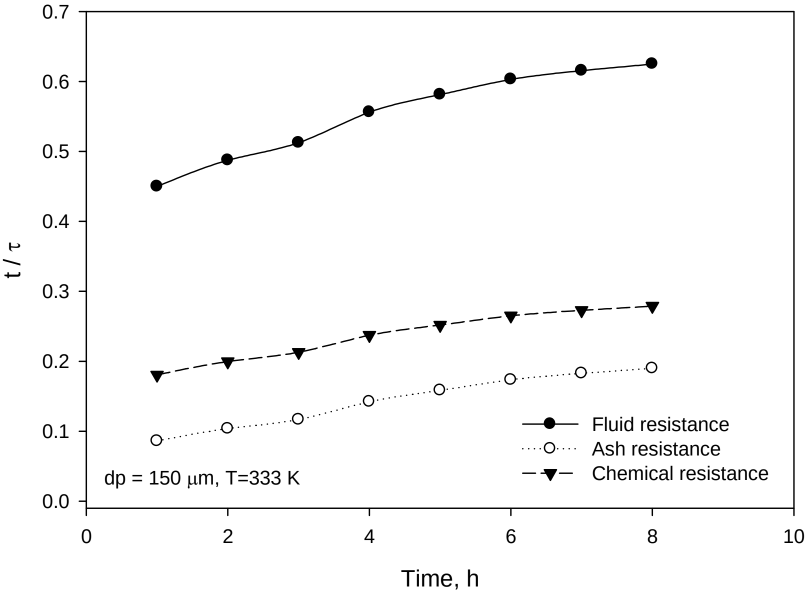

Fig. 4.23 t/τ for fluid, ash and chemical resistance versus time at 150μm particle size and 333 K temperature

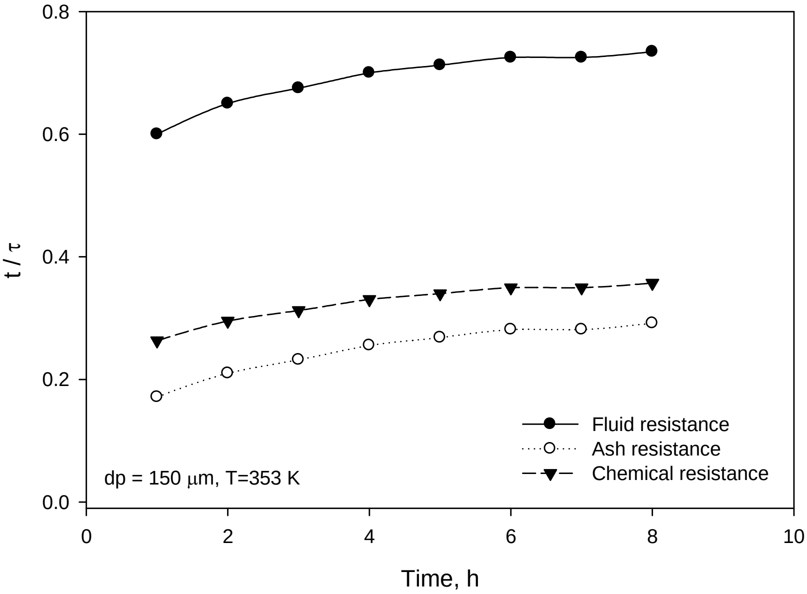

Fig. 4.24 t/τ for fluid, ash and chemical resistance versus time at 150μm particle size and 353 K temperature

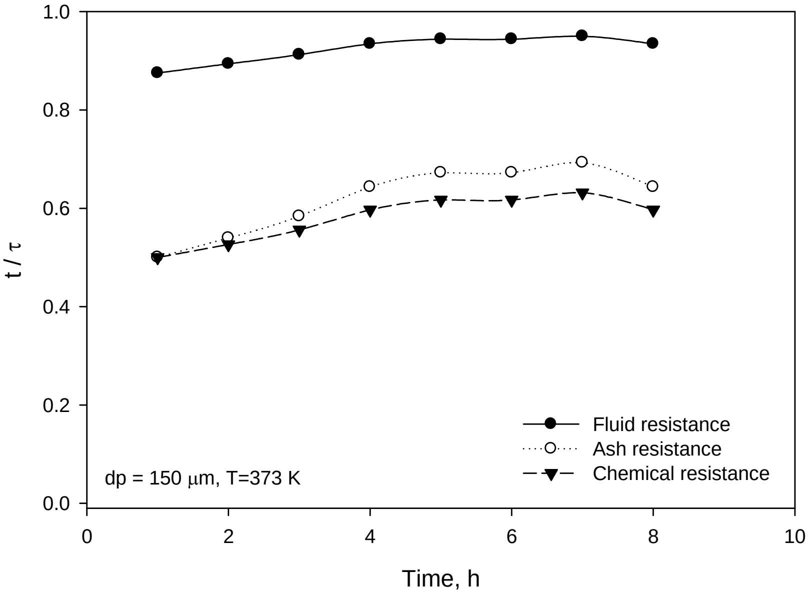

Fig. 4.25 t/τ for fluid, ash and chemical resistance versus time at 150μm particle size and 373 K temperature

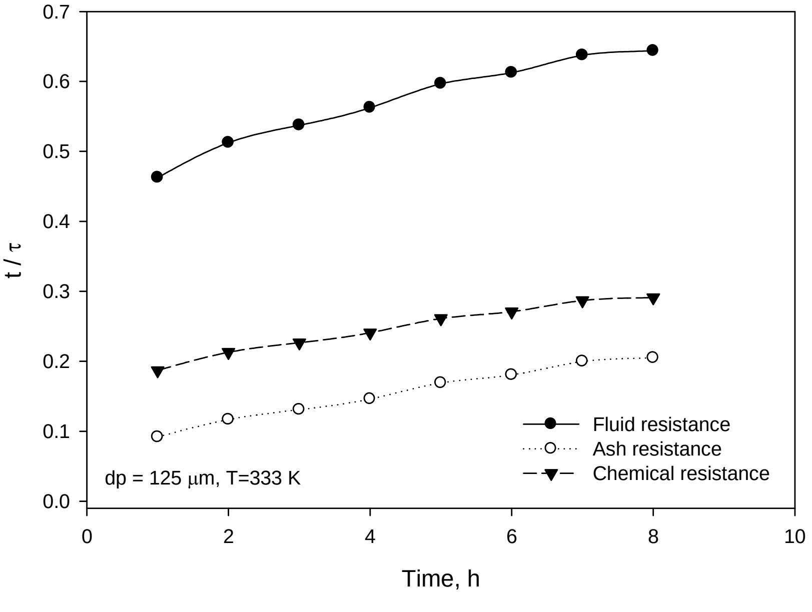

Fig. 4.26 t/τ for fluid, ash and chemical resistance versus time at 125μm particle size and 333 K temperature

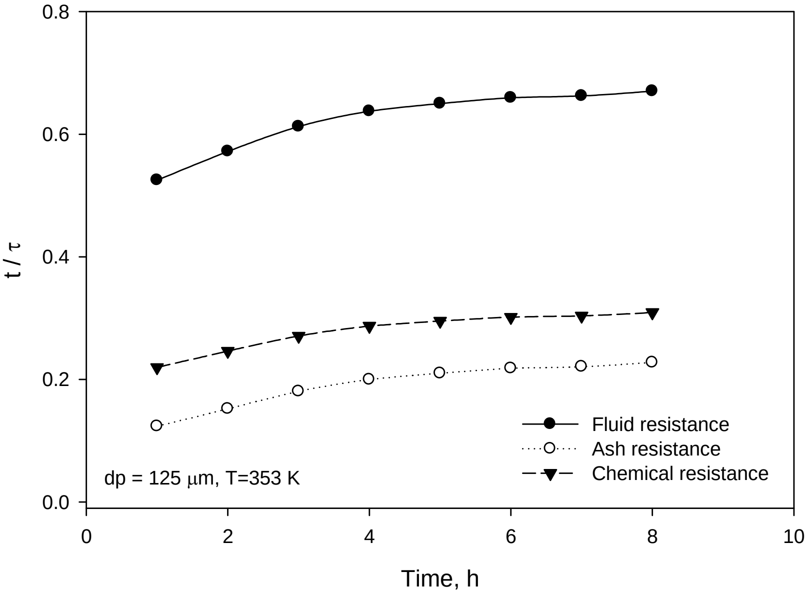

Fig. 4.27 t/τ for fluid, ash and chemical resistance versus time at 125μm particle size and 353 K temperature

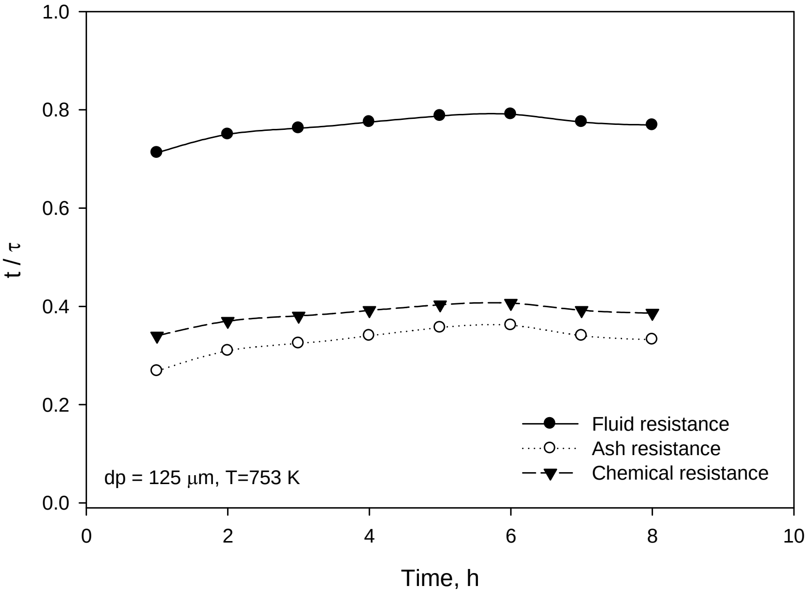

Fig. 4.28 t/τ for fluid, ash and chemical resistance versus time at 125μm particle size and 373 K temperature

The time required for complete conversion for film diffusion (Eq. 3.7), for ash diffusion (Eq. 3.16) and for chemical reaction (Eq. 3.22) are given in the following equations:

$$\tau = \frac{\rho_B R}{3bk_g C_{Ao}} \qquad \text{...(3.7)}$$

$$\tau = \frac{\rho_B R^2}{6bD_e C_{Ao}} \qquad \text{...(3.16)}$$

$$\tau = \frac{\rho_B R}{bkC_{Ao}} \qquad \text{...(3.22)}$$

The undetermined values of $\frac{\rho_B}{3bk_g}$, $\frac{\rho_B}{6bD_e}$ and $\frac{\rho_B}{bk}$ can be estimated from calculated values of time form complete conversion and they were plotted versus time as shown in Figures 4.20 to 4.28.

Where R is particle size, ρ_B is molar volume, k_g is mass transfer coefficient, C_{Ao} is initial concentration (0.216), D_e is effective diffusivity and k is the rate constant for the surface reaction.

From these figures, it is obvious that as time increase the value of these undetermined decreases where in Figures 4.29 to 4.31 at temperature of 373 K the curve decrease sharply as time increase, this because the value of molar volume affected with time while the value of mass transfer coefficient affected only with temperature.

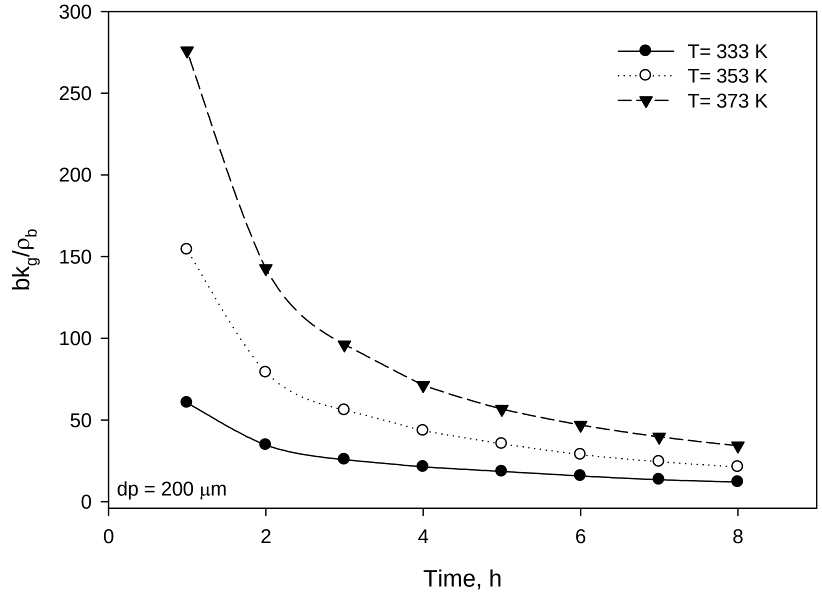

Fig. 4.29 bk_g/ρ_b versus time at different temperatures and 200 μm particle size

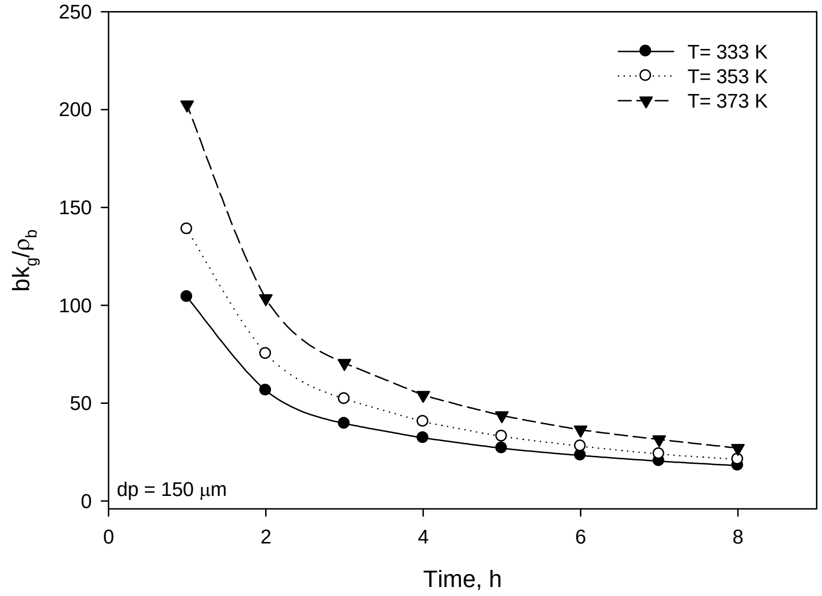

Fig. 4.30 bk_g/ρ_b versus time at different temperatures and 150 μm particle size

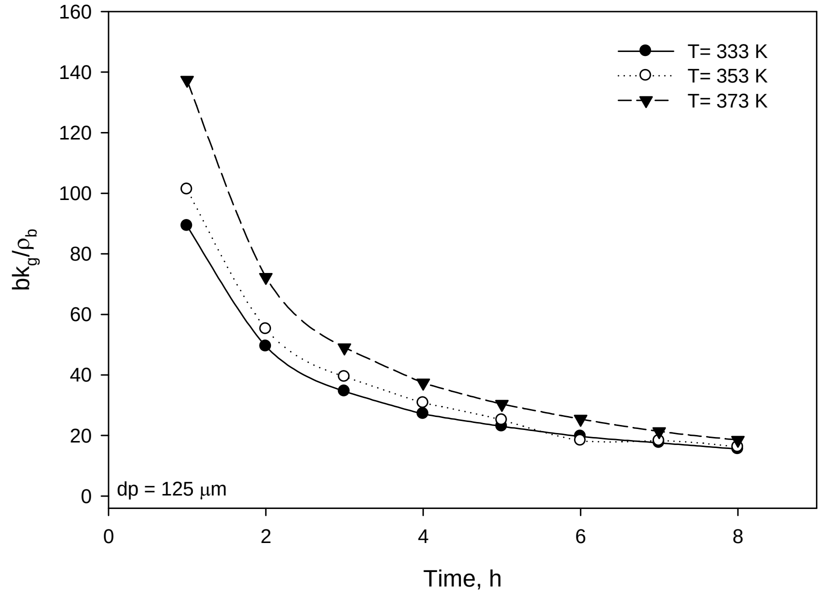

Fig. 4.31 bk_g/ρ_b versus time at different temperatures and 125 μm particle size

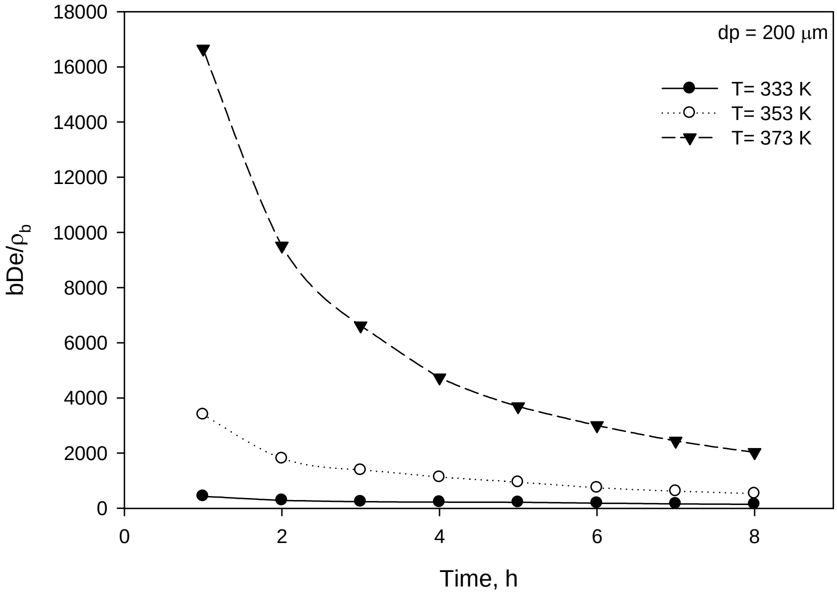

Fig. 4.32 bDe/ρ_b versus time at different temperatures and 200 μm particle size

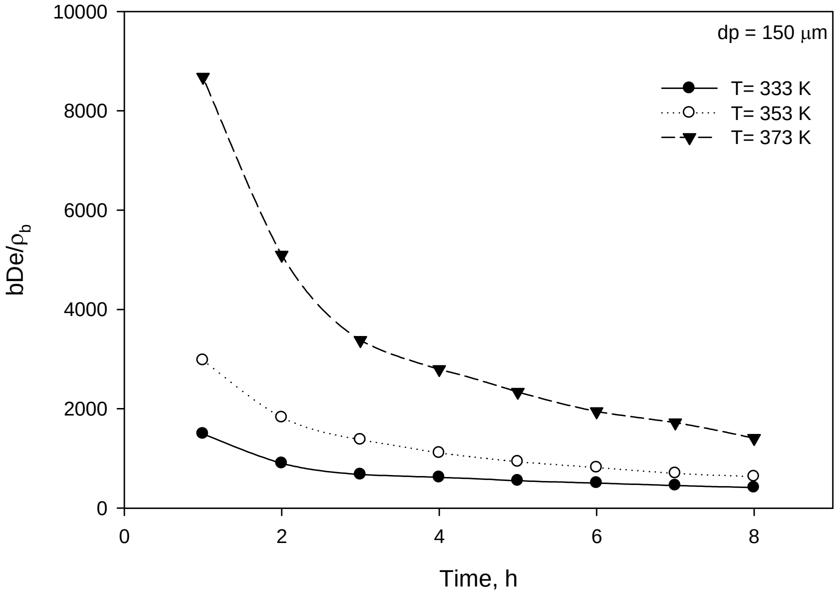

Fig. 4.33 bDe/ρ_b f versus time at different temperatures and 150 μm particle size

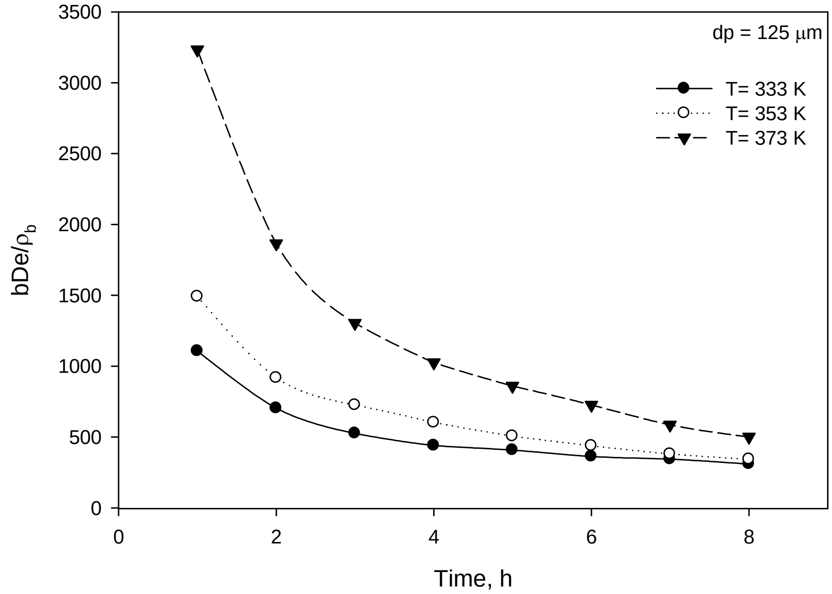

Fig. 4.34 bDe/ρ_b versus time at different temperatures and 125 μm particle size

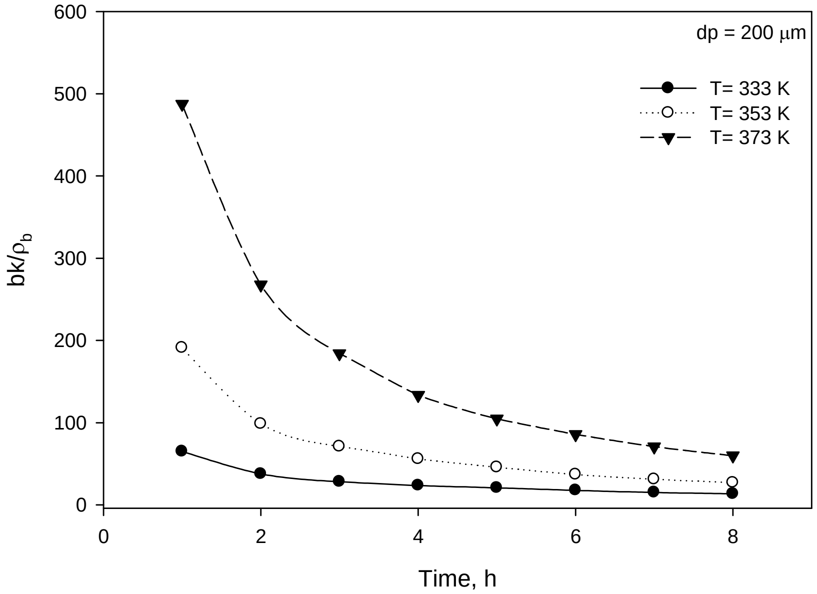

Fig. 4.35 bk_g/ρ_b versus time at different temperatures and 200 μm particle size

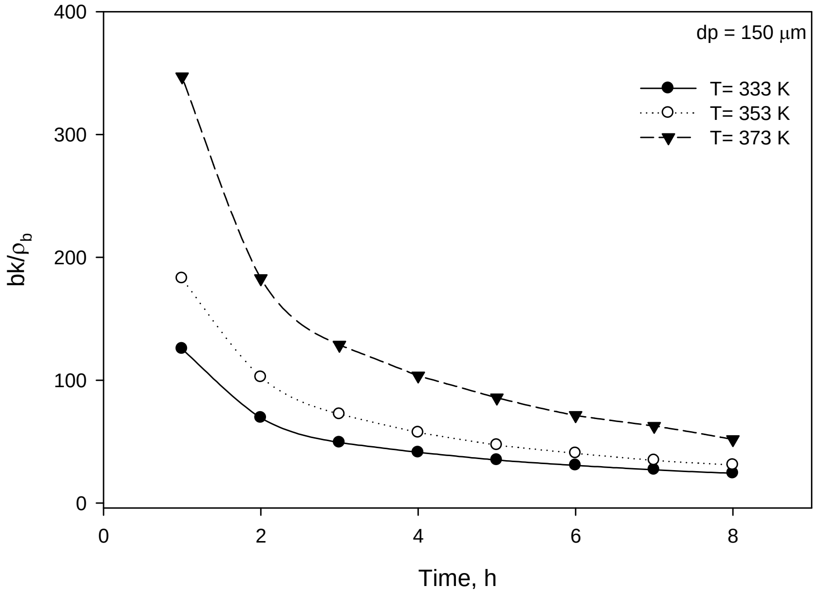

Fig. 4.36 bk_g/ρ_b versus time at different temperatures and 150 μm particle size

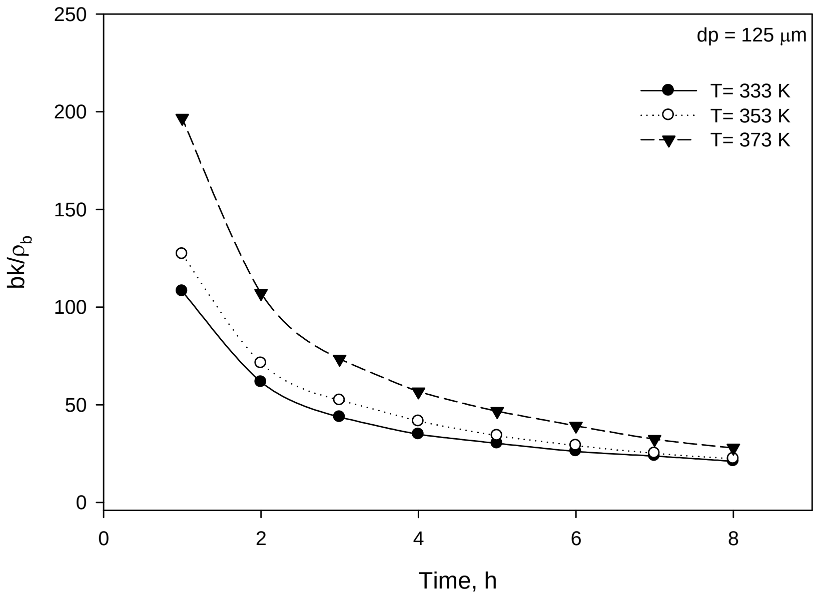

Fig. 4.37 bk_g/ρ_b versus time at different temperatures and 125 μm particle size

Figures 4.32 to 4.34 also show a sharply decrease of the values of $\frac{bD_e}{\rho_B}$ with time where this decrease results from the effect of molar volume while the effective diffusivity affected only with temperature.

Examining Figures 4.35 to 4.37, the same decrease of the values of $\frac{bk}{\rho_B}$ as the previous figures, the sharply decrease of these values with time results from the change in molar volume with time while the rate constant for surface reaction affected only with temperature.

4.4 Kinetic Model of Vanadium with NaOH

The reaction kinetics has been studied according to the differential method of analysis. This method deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative *d(concentration)/d(time)*, and testing the goodness of the fit of equation with experiments.

The rate of reaction of the present work can be expressed according to following:

$$r_A = \left(\frac{dC_A}{dt} \right) = kC_A^n \qquad \ldots(4.8)$$

Where *k* is the rate coefficient and *n* is the order of the reaction.

Differential analysis of the complete rate equation [Levenspiel, 1999] was used to calculating the change of conversion with time from a given data as shown in equations below.

$$C_A = C_{Ao}(1 - X_A) \qquad \ldots(4.9)$$

Substitute in to Equation 4.8.

$$r_A = \left(\frac{dC_A}{dt} \right) = -kC_{Ao}^n (1 - X_A)^n \qquad \ldots(4.10)$$

And then:

$$\frac{dC_A}{dt} = -C_{Ao}\frac{dX_A}{dt} \qquad \ldots(4.11)$$

Substitute in Equation 4.10.

$$-C_{Ao}\frac{dX_A}{dt} = -kC_{Ao}^{n}(1 - X_A)^n \qquad \ldots(4.12)$$

$$\frac{dX_A}{dt} = kC_{Ao}^{n-1}(1 - X_A)^n \qquad \ldots(4.13)$$

Let $k' = kC_{Ao}^{n-1}$, so that Equation 4.13 becomes

$$\frac{dX_A}{dt} = k'(1 - X_A)^n \qquad \ldots(4.14)$$

Where $\frac{dX_A}{dt}$ is the conversion change with time.

Plotting of conversion at given particle size versus time and this plot gives second order polynomial equation, deriving these equations gives differential equation of $\frac{dX_A}{dt}$ that can be calculate from given data.

Taking natural logarithm of Equation 4.14 gives:

$$\ln\frac{dX_A}{dt} = \ln k' + n\ln(1 - X_A) \qquad \ldots(4.15)$$

Figures 4.38 to 4.46 show straight line of $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ with slope n and intercept $\ln k'$. The calculated values of n and k' are shown in Table 4.4.

The average value of the vanadium conversion reaction order (n) is minus 3.42 (about $-\frac{10}{3}$) and the values of rate coefficient appear to increase with temperature.

Table 4.4 Calculated values of k' and n versus various reaction conditions

Temp. (K)	*dp*, µm	k'	n
333	200	0.910	-3.3295
353	150	0.945	-3.4266
373	125	0.968	-3.9122
333	200	0.930	-3.1324
353	150	0.966	-3.1611
373	125	0.989	-3.4403
333	200	0.949	-3.1903
353	150	0.985	-3.0303
373	125	1.009	-3.3684

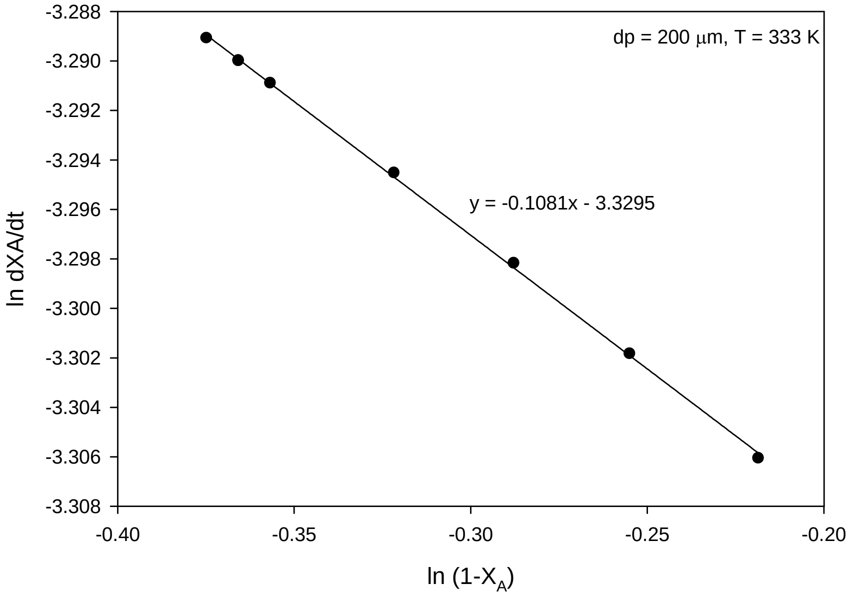

Fig. 4.38 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 333 K temperature and 200 μm particle size

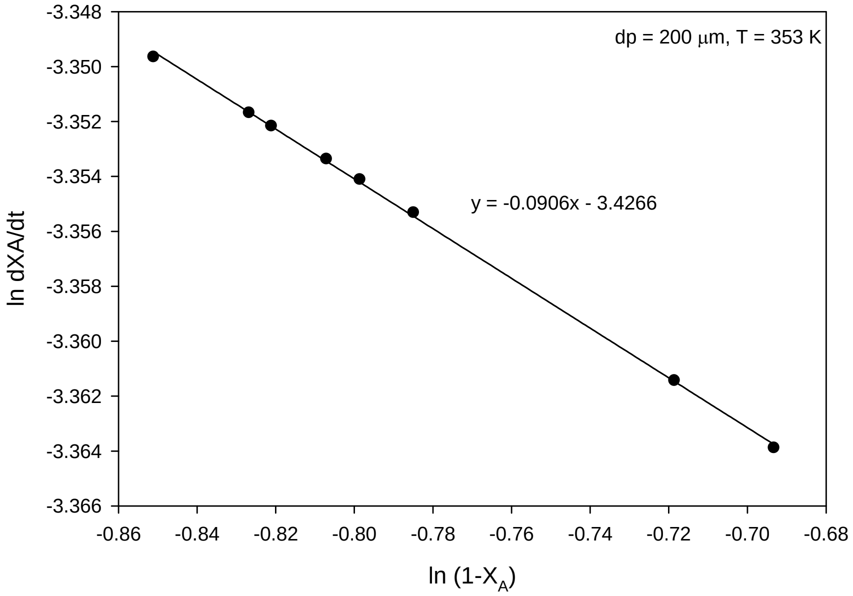

Fig. 4.39 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 353 K temperature and 200 μm particle size

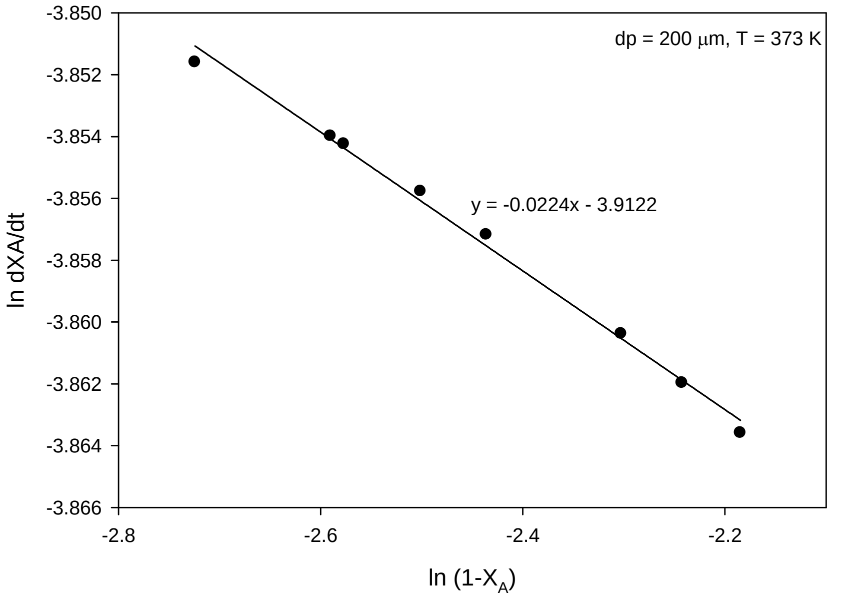

Fig. 4.40 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 373 K temperature and 200 μm particle size

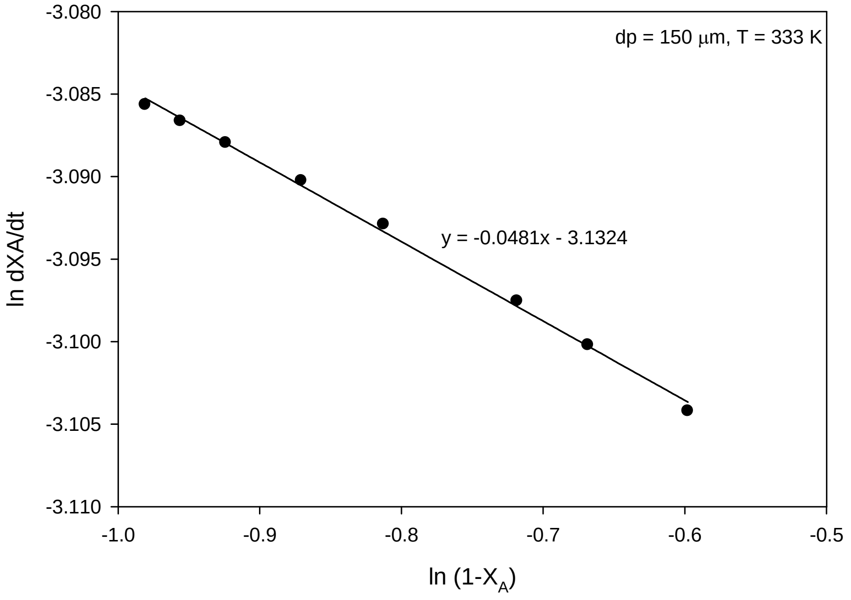

Fig. 4.41 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 333 K temperature and 150 μm particle size

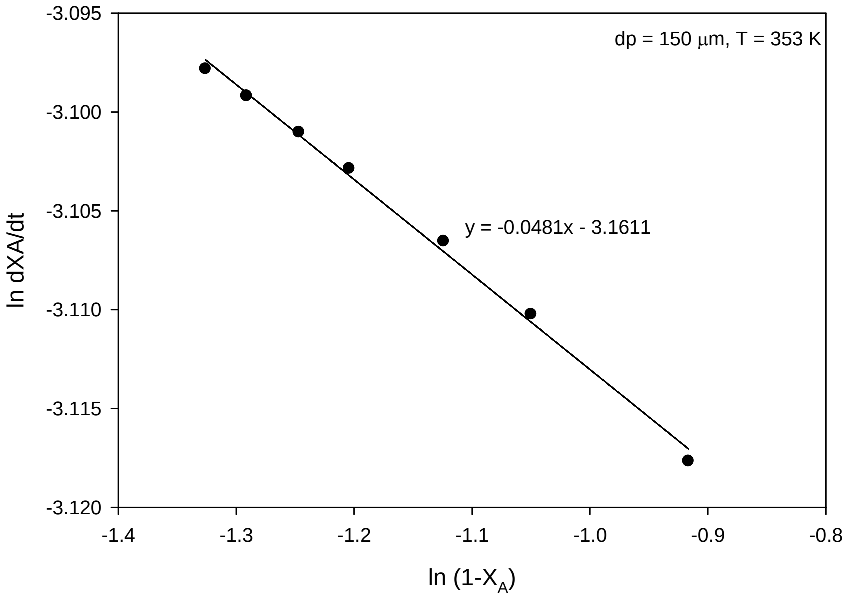

Fig. 4.42 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 353 K temperature and 150 μm particle size

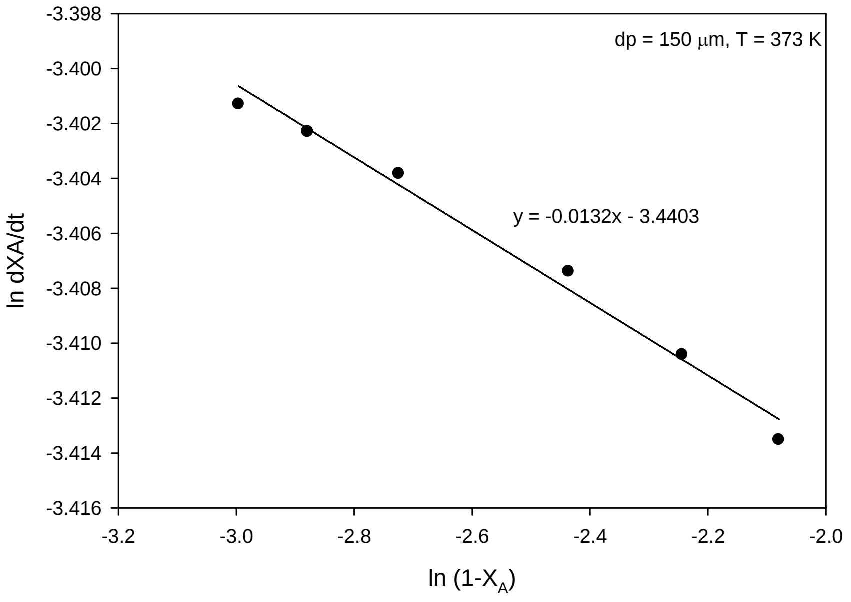

Fig. 4.43 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 373 K temperature and 150 μm particle size

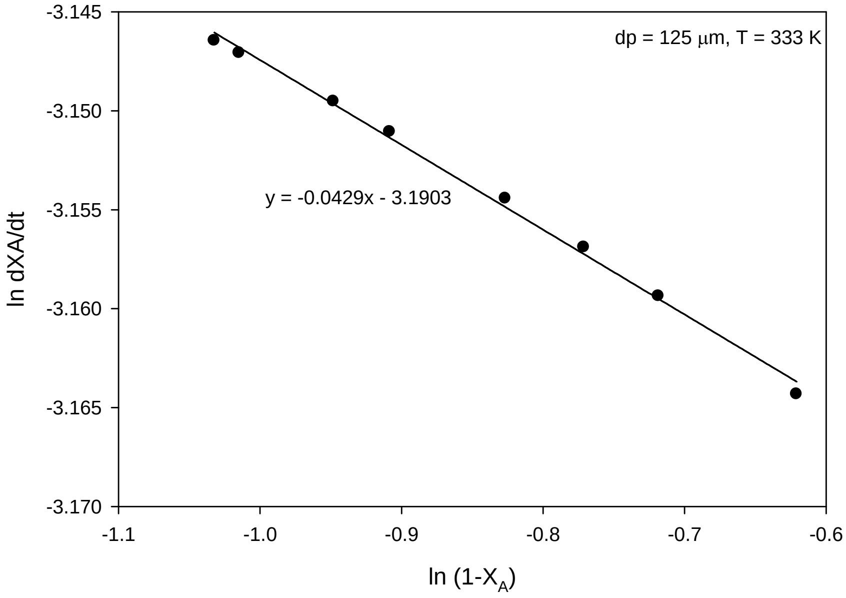

Fig. 4.44 $\ln \frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 333 K temperature and 125 μm particle size

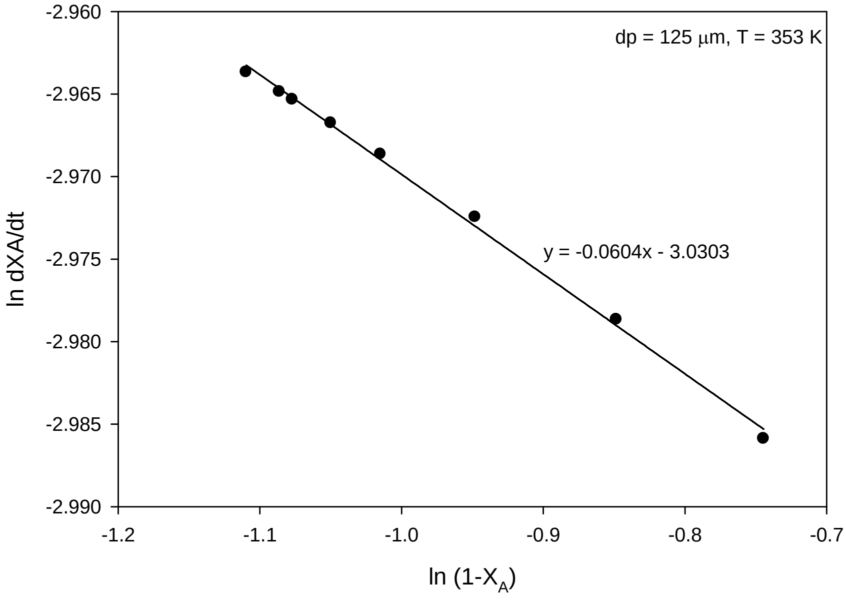

Fig. 4.45 $\ln \frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 353 K temperature and 125 μm particle size

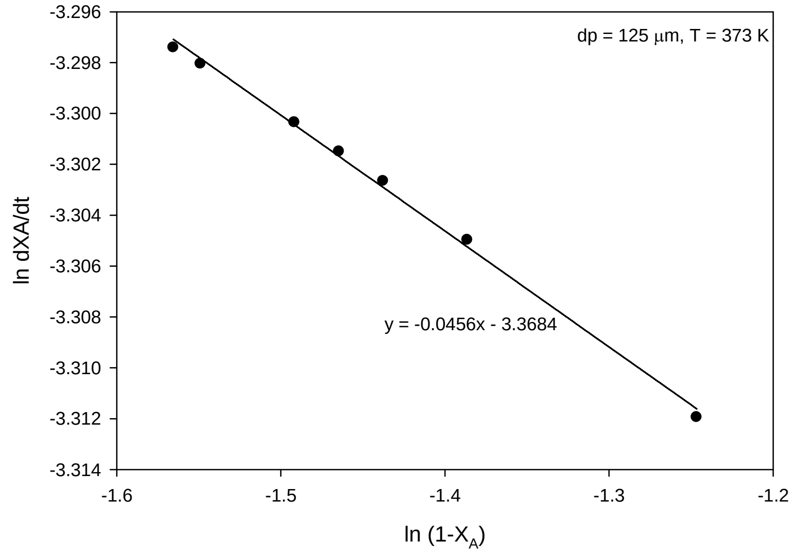

Fig. 4.46 $\ln\frac{dX_A}{dt}$ versus $\ln(1-X_A)$ at 373 K temperature and 125 μm particle size

The rate coefficients can be expressed by Arrhenius law, which it is a function of temperature and particle size and assuming that the change of *k* versus *dp* at same temperature is done according to power low as in the below equation.

$$k = f(T)f(dp) \qquad \text{...(4.16)}$$

$$k = A_o \exp\left(-\frac{E}{RT}\right)dp^m \qquad \text{...(4.17)}$$

Where:

m = constant

A_o= pre-exponential constant (frequency factor)

E = activation energy of the reaction.

R = gas universal constant.

T = absolute temperature.

Non-linear estimation method has been used for solving Equation 4.17 to obtain the values of m, A_o and E. The calculated values are illustrated in Table 4.5.

Table 4.5 Calculated values of m, A_o and E

m, -	-0.1309
A_o, h^3(wt. %)^4	2.6884
E/R, -	129.87
E, J/mole	1080

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Based on the present work, the following points can be conclude:

1. A second order polynomial mathematical correlation was employed in the range of independent variables temperature. X_1 (60 to 100° C), particle size X_2 (125-200 μm), time X_3 (up to 8 hours) with correction of 0.9990 and variance of 0.9981 and confidence levels of 95 %.
2. It was found that vanadium conversion affected clearly by increasing temperature and leaching time and reducing Particle size of the ash.
3. It was found that the chemical reaction has the highest resistance among other steps, which could consider as the controlling step for vanadium recovery by treatment with caustic soda.
4. A complete vanadium conversion achieved at 5 hours, 125 μm piratical size of ash at 373 K, while 7 hours was required to get such conversion for the 125 μm particle size ash at 373 K.
5. Vanadium conversion was found to be minus third orders with activation energy of 1080 J/ mole and frequency factor of about 2.6884

5.2 Recommendations

1. More researches should be carried out to find more accurate model to describe the leaching process by caustic soda to separate vanadium from fly ash.
2. Study of vanadium recovery process by $Ca(OH)_2$ leaching.
3. Experimental and Theoretical investigations could be carried out on recovery of vanadium from different ash sources obtained from various oil-firing systems.

REFERENCES

- Agers, D. W., U. S. patent 3,415,616 (1968).
- Akita, S. Maeda, T. and Takeuchi, H., J. Chem. Tech. and Biotech, **62** (4), 345 (1995).
- Al-Duhan, A., "*Inorganic Study of the Extraction of Vanadium (IV)*", Ph. D. thesis (1996).
- Anderson, R. T., Vrionis, H. A. and Lovely, D. R., "*Vanadium Respiration by Geobacter Metallireducens*", University of Massachusetts, Massachusetts (2004).
- Barbooti, M. M. and Al-Madfai, S. H., Thermo. Chem. Acta, 126, 43 (1988).
- Basharwar, A. N., "*Kinetic Invariant Model of Dissolution with Chemical Reaction*", **37** (3), (1991).
- Boucher, D. F. and Brier, S. C., Trans. Amer. Inst. Chem. Eng., 300, 697 (1942).
- Brook, P. T., Nichos, I. L. and Potter, G. M., "*Vanadium Recovery from Dolomitic*", Nevada Shale, New York, February (1971).
- Cole, C. E. and Spence, D. J., U. S. patent 3,520,650 (1970).
- Corigilano, F., DiPasquale S., and Primerano, P., *"Method for Producing High Purity Vanadium"*, part No. 5, 587, 132 (1989).
- Costigan, M. and Cray, R., *"Health and Safety Executive"*, Liverpool, UK.
- Cotton, F. A. and Wilkinson, G., "*Advanced Inorganic Chemistry*", 5th edition, New York (1988).
- Florence, T. M. and Farrar, Y. S., Aust. J. Chem., 22 (2), 473 (1969).

- Friedman, R. H., Getty Oil Company, 06137, 304, August, 3, (1986).
- Gupta, C. K. and Krishnamutthy, *"Extractive Metallurgy of Vanadium"*, Elsevier Science Publishers, (1992).
- Hansen, D. J., Fodd, J. B. and Malacrne, O. J., Colorado Mining Assoc. Mining Yearbook, pp 141-149, 1987.
- Hobson, G. D., "*Modern Petroleum Technology*", 5th edition, Institute of Petroleum, London (1979).
- House, J. E., "*Solvent Extraction Chemistry*", North Holland Co., Amsterdam (1967).
- Izumi et al., J. Chem. Eng. Jap., 20, 505 (1987).
- Jackson, E., "*Hydrometallurgical Extraction and Reclamation*"
- Jalhoom, M. G., First Symposium on Utilizing of Neutral Resources and the Production of Alternative Materials, Iraq-Baghdad, June (1992).
- Jasim, S. A., "*Study of the Extraction of Vanadium by TBP*", M. Sc. Thesis (1998).
- Jones, K. H., "*Vanadium*", Bear Metallurgical Company, Florida, Oct. 29 (2002).
- Judd, J. C., Sandbarg, R. G. and Huiah, J. L., Rep. Invest. US. Br. Mines-9025 (1986).
- Khorfan, S. Wahoud, A. and Reda, Y., "*Recovery of Vanadium Pentoxide from Spent Catalyst Used in the Manufacture of Sulfuric Acid*", Atomic Energy Commission Hydrometallurgy Office, Damascus, Dec. 10 (2002).
- Kirk, R. E. and Othmer, D. E., "*Encyclopedia of Chemical Technology*", 3rd edition, John-Wiley and Sons (1983).

- Kunii, D. and Levenspiel, O., "*Fluidization Engineering*", 2nd edition, Butter Worth, Boston, MA (1991).
- Levenspiel, O., "*Chemical Reaction Engineering*", 3rd edition, John-Wiley and Sons Inc., New York (1994).
- Lucas, B. H. and Ritcey, G. M., "*An Alkaline Roast-leach Process*", Toronto (1977).
- Malone, D. P. and Holcambe T. C., Petroleum V-C Ashland, part No. 6, 231, 640, May 15, (2001).
- Mefos, G. Ye, *"Pyrometallurgyical Processing of Vandiferrous Slag Using Plasma Induction Heating"*, **vol. 1**, pp 225-231 (1992).
- Merrit, R. C., "*The Extraction Metallurgy of Uranium*", Colorado School of Mines Research Inst., Colorado (1971).
- Monashi, J., Rappas, A. S. and Douglas, D. A., Metallurgical Transaction, **Vol. 7B**, pp 115-118 March (1981).
- Mousa, K. M., "*Study of Leaching on Recovery of Vanadium from Scale Resides of Oil-fired Power Station*", M. Sc. Thesis (1999).
- Ottertum, H. and Strdell, E., Proceeding of the International Solvent Extraction Conference (ISEC)-77, Torento (1977).
- Perry, R. H. and Chilton, C. H., "*Chemical Engineer Handbook*", 5th edition, McGraw-Hill Book Co., New York (1973).
- Ressel, R., Hochemhofer, M. and Antrekowitsch, H., *"Metallutgy of non-ferrous Metals"*, Leobenll, 8700, Autria.
- Rickles, N., Chem. Eng., March (1965).
- Rigg, T. and Garner, J. O., J. Inorg. Nucl. Chem., 29, (1967).

- Ritecy, G. M. and Ashbook, A. W.,"*Solvent Extraction Principles and Application to Process Metallurgy*", Amsterdam (1979).
- Rosenbum, J. B., "*Vanadium Ore Processing*", annual Meeting (1971).
- Sato, T., Ikomas, J. and Nakamura, T., Hydrometalurgy, 6 (1,2), 13 (1980).
- Sato, T., Ikomas, J. and Nakamura, T., J. Inorg. Nucl. Chem., 39, 395 (1977).
- Sato, T., Kotani, S. and Terrao, O., Proceeding of the International Solvent Extraction Conference,
- Smith, J. M., "*Chemical Engineering Kinetics*", 3rd edition, McGraw-Hill Book Co. (1981).
- Swanson, R. R., U. S. patent, 34646784 (1969).
- Tedesco, P. H. and DeRumi, V. B., J. Inorg. Nucl. Chem., **42**, 269 (1980).
- Treybal, R. E., "*Mass Transfer Operation*", McGraw-Hill Book Co. (1955).
- Wen, G. Y., "*Non-catalytic Heterogeneous Solid Fluid Reaction Model*", Ind. Eng. Chem., **60** (9), 34 (1968).
- Yagi, S. and Kunii, D., Chem. Eng. Sci., **16**, 364 (1961).

الخلاصة

اهتم هذا البحث بدراسة حركية استعادة الفناديوم من مخلفات حرق الوقود في محطات الطاقة الكهربائية بعملية الاستخلاص بواسطة هيدروكسيد الصوديوم من نتائج البحث السابق لموسى (١٩٩٩). البيانات المحددة تم اختيارها عند حجم حبيبي يتراوح من ١٢٥ الى ٢٠٠ مايكرومتر ودرجة حرارة من ٣٤٣-٣٧٣ كلفن و وقت زمن الهظم من ١-٨ ساعات وتركيز مولاري ثابت تراوح من ٣-٤ مولاري .

تشير النتائج الى ان نسبة استعادة الفناديوم تزداد بزيادة درجة الحرارة وزمن الهظم ونقصان الحجم الحبيبي . استخدمت معادلة رياضية من الدرجة الثانية لوصف استجابة استعادة الفناديوم و وجد ان معامل الارتباط كان ٠.٩٩٩٠ والتباين ٠.٩٩٨١ لمستوى ثقة ٩٥ %.

دراسة الحركية اظهرت ان الخطوة المسيطرة على العملية هي التفاعل الكيمياوي و التي تمتلك اكبر مقاومة من بين باقي الخطوات وتم الحصول على استعادة تامة للفناديوم بوقت ٧ ساعات. كانت درجة حركية التفاعل هي -٣ و طاقة تنشيط ١٠٨٠ جول لكل مول وعامل تردد ٢.٦٨٨٤.

دراسة حركية استعادة الفناديوم من مخلفات حرق الوقود في محطات الطاقة الكهربائية

رسالة
مقدمة إلى كلية الهندسة في جامعة النهرين وهي جزء من متطلبات نيل
درجة ماجستير في علوم الهندسة الكيمياوية

من قبل
رنا خالد عبيد
(بكالوريوس في الهندسة الكيمياوية ٢٠٠٤)

محرم ١٤٢٩
كانون الثاني ٢٠٠٨