Experimental and Kinetics of Vanadium Recovery from Spent Catalyst

Using Caustic Soda

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

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B.Sc. in 2006

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Certification

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Abstract

A Theoretical and experimental investigation was conducted to study recovery of vanadium from spent catalyst via leaching process using sodium hydroxide to investigate the effect of process variables on vanadium recovery and study kinetic of recovered was investigated by determining the controlling step.

The effect of process variables (temperature, particle size, molarity of sodium hydroxide and leaching time)on the percentages of vanadium recovery were investigated and it was found that the percentage of vanadium recovery increased with:

- Increasing the temperature up to 100 ℃ ,
- Increasing sodium hydroxide molarity in the rang (2 to 4M),
- Increasing leaching time,
- Decreasing particle size from (200 to 100 µm).

A complete vanadium recovery was achieved at the following conditions:

- Temperature (100˚C), particle size (100 µm), molarity of NaOH (4 molar), and time (5 hours).

A second order polynomial mathematical correlation was employed in the range of independent variables temp. X_1 (60˚C - 100˚C), X_2 particle size (100 µm - 200 µm), time X_3 up to 5 hr and molarity X_4 between (2M and 4M) with correction factor of 0.9890 .

The kinetic study shows that the Chemical reaction is the controlling step due to the highest resistance among the other steps (Fluid film and Ash layer).

Contents

List of Symbols

Symbols	Notations
C_A or C_B	Concentration of reactant (kmol/m^3)
C_{A0}	Initial Concentration of component A (kmol/m^3)
D	Impeller diameter (m)
D_e	Effective diffusivity (m^2/s)
k_g	Mass transfer coefficient (m /s)
M	molarity (mol /ℓ)
$N_A$orN_B	Number of moles of component A or B at any time
Q	Rate of mass transfer (kmol/$m^3.s$)
$\mathcal{Q}_A$	Flux of A through the surface at any radius (r), kmole/$m^3.s$
$\mathcal{Q}_{AS}$	Flux of A through the exterior surface of particle, kmole/$m^3.s$
$\mathcal{Q}_{AC}$	Flux of A through the exterior surface of particle, kmole/$m^3.s$
R	Radius (m)
r_c	Radius of unreacted core (m)
S_{ex}	External surface area (m^2)
T	Temperature (K)
t	Time (s)
V	Volume (m^3)

X	Conversion
Y	Percentage of vanadium recovery, %

Greek Letters

Symbols	**Notations**
ρ_B	Molar Density (kmol / m^3)
τ	Time for complete conversion (s)
E	Correlation error

Abbreviations

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

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Figure Title Page

Vanadium is a natural element in the earth. It is a white to gray metal, often found as crystals. It has no particular odor. Vanadium occurs naturally in fuel oils and coal. In the environment it is usually combined with other elements such as oxygen, sodium, sulfur, or chloride. The forms of vanadium most likely to be found at waste sites are not well known. One manmade form, vanadium oxide (vanadium bound to oxygen), is most often used by industry, mostly in making steel. Vanadium oxide can be a yellow-orange powder, dark-grey flakes, or yellow crystals. Much smaller amounts are used in making rubber, plastics, ceramics, and certain other chemicals. vanadium can get into the air, soil, groundwater or surface water, the most likely way for the chemical to get into the air is when fuel oil is burned, When rocks and soil containing vanadium are broken down into dusts by wind and rain, in water it does not dissolve well but it can be carried by the water much as particles of sand might be carried [William L. Roper, 1992] .

In 1801, del Rio discovered Vanadium, although a French chemist dismissed his discovery claiming he had merely found impure chromium. Believing the French chemist, Del Rio accepted his finding. It was not until 1830, that Sefstrom rediscovered the element and named it after the Scandinavian goddess Vanadis, due to its attractive multicolored compounds. However it was not until 1867, that Roscoe reduced the chloride with hydrogen to isolate the first sample of vanadium. It took another 60 years before vanadium was produced with purities as high as 99.3 to 99.8%[Dobson, 2001].

Vanadium is a chemical element that has the symbol V and atomic number 23 with an atomic mass of 50.942, a melting point of 1890 ± 10 °C, a boiling point of 3380 °C at 1 atm (1.013×10^5 Pa), and a specific gravity of 6.11 at 18.7 °C [Weast, 1986-87]. Soft and ductile element, Vanadium has a very low and non-accumulative toxicity; recovery plants can be operated is such manner to ensure no air pollution results [Kirk and Othmer, 1983].

Vanadium can exist in different oxidation states from -2 to +5 but the forms found in natural environment state +3, +4 and +5. Oxidation state +4 is the most stable. Compounds of vanadium may contain vanadium in oxidation states of -1, 0, +2, +3, +4, and +5. Vanadium is usually found bound to oxygen as a negatively charged polymeric oxyanion that tends to complex to polarizable ligands, such as phosphorus and sulfur [Buckingham, 1973; Cotton & Wilkinson 1980].

Vanadium is employed for the manufacture of a variety of vanadium compounds. Vanadium compounds have been found effective for catalyzing both organic oxidation and reduction. The oxides of vanadium have found many applications as catalysts especially in vapor-phase reductions. Vanadium pentoxide is the most common commercial form of vanadium that is dissolves in water and acids forming vanadates with bases, It is the source of vanadium used in the manufacture of ferrovanadium. It can be used as a dye and color-fixer, and it’s used as a catalyst principally in the production of sulfuric acid by Contact Process that involving the catalytic oxidation of sulfur dioxide, SO_2, to sulfur trioxide, SO_3. Vanadium catalyst (vanadium (V) oxide) is also used in this reaction as speeding the rate of the reaction. $2SO_2\,(g) + O_2\,(g) \text{----->} 2SO_3\,(g)$

Catalysts based on vanadium pentoxide are widely used in the conversion of naphthalene to phthalic anhydride. Vanadium is also used as catalyst in the process of CO_2 removal from the gas mixture in ammonia synthesis. Vanadyl sulfate $VOSO_4$, also called vanadium(IV) sulfate oxide hydrate, is used as a relatively controversial dietary supplement, primarily for increasing insulin sensitivity and body-building . [West et al, 1987].

Recovery of vanadium can be achieved by extraction with acids and alkalins from scales and ashes or it could be recovered by amine solvent extraction from ores and slag. 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[M. Jalhoom, 1992].

There are many of researcher study recovery of vanadium from spent sulphuric acid catalysts, which in turn are employed to prepare catalysts such as hydrocarbon oxidation catalysts and catalysts for the manufacture of sulphuric acid [Lozano & Juan, 2001] stated that vanadium could be recovered from sulfate solutions derived from the leaching of spent catalysts by means of solvent extraction with primary aliphatic amine. [Otternum & Strandel, 1979] described a process for the recovery of vanadium from sulfate leaching solution using organic phase containing di(2-ethylhexyl) phosphoric acid combined with tributyl phosphate. [HO et al.] compared the di(2-ethylhexyl)phosphoric acid and amine extractants and investigated the relative extracting performance of quaternary amine in the case of a range of vanadium (V) anionic species between pH 6 and 13. [Uhlemann, E. et al., 1990] Alkaline leaching is more selective for iron but dissolves some silica and is more costly in terms of reagent. [Ikeyama et al., 1987] describes a process in which vanadium and molybdenum were recovered as sodium vanadate [$(NH_4)_3VO_4$] and H_2MoO_4, with yields of 96% and 92%, respectively. [S. Khorfan , A.Wahoud and

Y. Reda , 2002] using a three-step process involving acid leaching ,oxidation and precipitation.Ahigh solid/liquid ratio in the leaching stage was used to obtain high concentration of vanadium pentoxide and low acid consumption that allowed direct precipitation without the use of extraction by rather expensive organic solvents. Sodium carbonate solution of one mole/liter concentration was used in the precipitation stage, Leaching efficiency of 96.6% was achieved and the concentration of vanadium in the spent catalyst was tested to be 0.187%. [L. D. Kurbatova and D. I. Kurbatov,2005] studied the extraction recovery of Vanadium(V) from Sulfuric Acid Solutions, where the IR and electronic absorption spectra of di-2-ethylhexyl hydrogen phosphate (HDEHP) extracts of vanadium(V) and sulfuric acid and of vanadium(V) solutions in sulfuric acid were studied. The composition of the extractable complex was determined, and the equation of vanadium (V) extraction with HDEHP was suggested. The equilibrium constant of vanadium (V) extraction from concentrated sulfuric acid solutions was found.

The aim of this Work:

The aim of this work is to explain the experimental data of vanadium recovery from spent catalyst used in the manufacture of sulphuric acid and study the effect of the following different variables such as : The effect of temperature on vanadium recovery, The effect of NaOH molarity on vanadium recovery, The effect of particle size on vanadium recovery, The effect of the contact time on vanadium recovery and Study kinetic of recovered vanadium by determining the controlling step of the recovery process.

2.1 Vanadium element and 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]. Vanadium is found in approximately 54 different minerals as well as phosphate rock, certain iron ores, some crude oils (in the form of complexes) and meteorites. Some of the more important minerals in which also include carnotite, roscoelite, vanadinite and patronite. Vanadium is ranked as the twelfth most aboundant metal (135ppm), thus considerably more aboundant than base metals like Ni,Zn,Cu,Pb and Sn as shown in figure (2-1) .

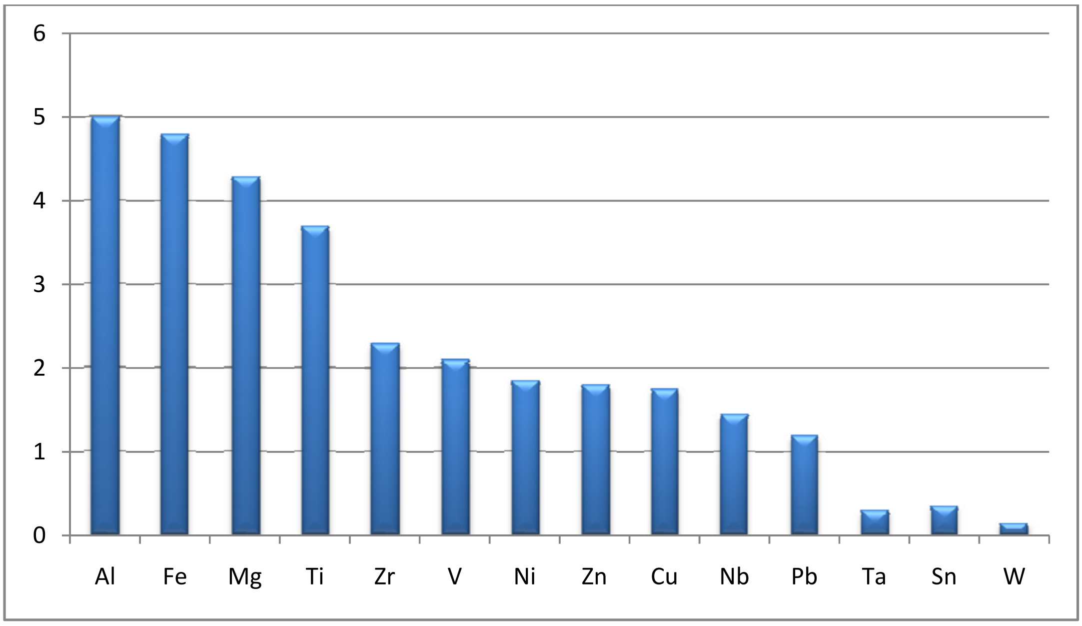

Figure (2-1): The abundance of vanadium and important metals on the earth [Gouzhu, 2006]

Seventy five V-containing minerals are known ; the states of valance differ among the minerals. The minerals can be diveded into seven categories ; oxides, phosphates, silicates, sulphates, sulphides, titanates ,vanadates . Although vanadium forms numerous minerals almost all of the world source are distributed in titaniferrous magnetite type deposit fig (2-2). Nearly 50% of the total vanadium source is distributed in titaniferrous magnetite type deposit. The estimated aggregated world vanadium sources are accounted to 56 300 000 tonnes . The world vanadium production until 1989 was about 917 000 tonnes which is about 1.64% of the deposited vanadium known so far , approximately 1.6% comes from titaniferrous magnetite. [Mikael Lindvall,2005]

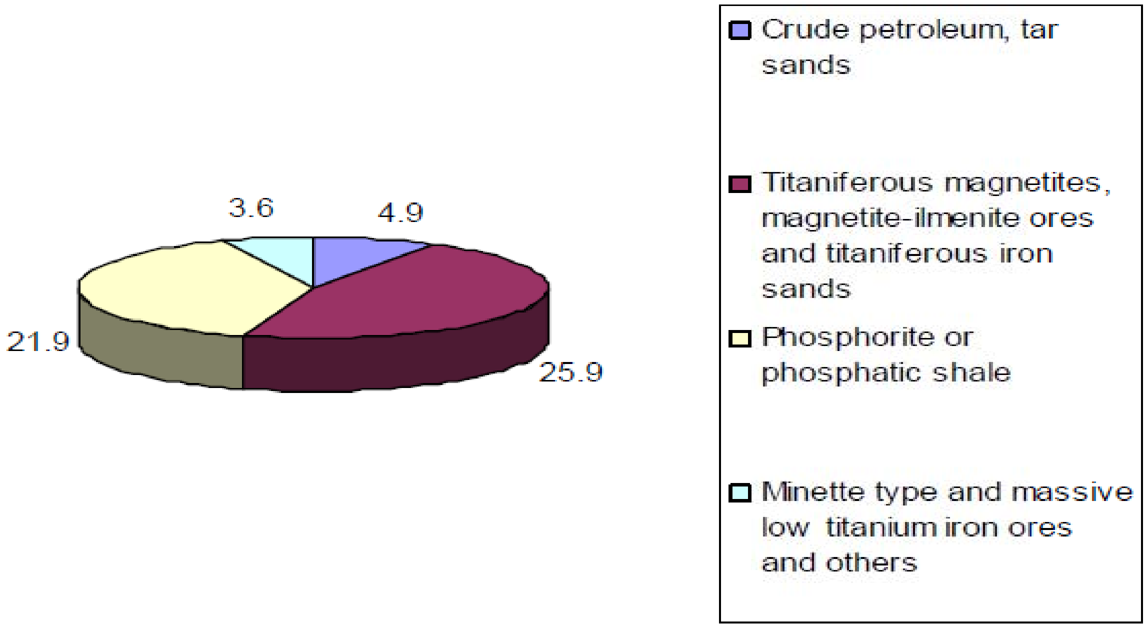

Figure (2-2) : Distribution of the world sources of vanadium in major deposit type in Mtoones [C.K Gupta & N.Krishnamurthy ,1992]

2.2 Vanadium Uses

Vanadium is indeed a 20th century miracle metal. As mankind strives to make products stronger, lighter, and safer and more fuel efficient there will be ever increasing demand for the metal and the need for significant increases in sustainable, cost effective vanadium production. Unlike other metals whose markets are fully developed, commercial production of vanadium only arose in the 1960s, and so new applications continue to be found for the metal'suseful chemical and physical properties. Its principal use is as a strengthening addition to carbon steel and high strength steels in structural applications, oil and gas pipelines, buildings and cars. Tool steels and stainless steel use are also important. Titanium aluminium vanadium alloys are used in aircraft components, air frames, rocket motors and gas turbines. Non-steel uses include superalloys, welding and hard-facing, magnets and alloys used in nuclear engineering and superconductors. Vanadium chemical catalysts are used in the manufacture of sulphuric acid, maleicanhydride, EPDR rubber and desulphurization of sour gas and oil. Steel will remain the key end-use market, although growth in aerospace alloys and the emergence of new uses for titanium-vanadium will see this sector grow the fastest [Tamlin and Smith ,2007].

2.3 Vanadium products and their applications

The main vanadium products are: V_2O_5, VN and ferrovanadium (FeV). V_2O_5 is the mainly used as catalyst in the chemical and polymer industry and for production of ferrovanadium, which is essentially used in the steel industry as a V-alloy. VN is used for direct alloying.

Vanadium is also used in a multiple varity of applications in advanced research industry. The Main applications of Vanadium are shown in (figure 2-3) It can be summarized as follows:

- FeV-alloy , mainly for the steel industry
- V_2O_5 , mainly as catalyst and for FeV-production
- V_2O_3 , mainly for FeV- production
- VN for direct alloying of V and N
- V-metal for use I Al-V-Ti alloy

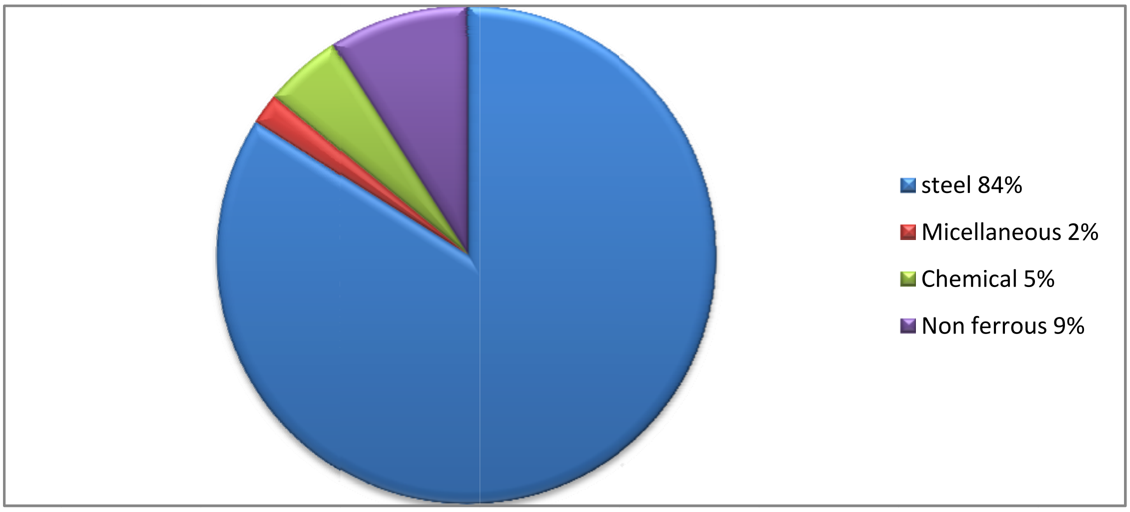

Figure (2-3): Distribution of various applications of vanadium[Gouzhu ,2006]

2.4 Vanadium Toxity

The toxicity of vanadium depends on its physico-chemical state; particularly on its valence state and solubility. Tetravalent $VOSO_4$ has been reported to be more than 5 times as toxic as trivalent V_2O_3 (Roschin, 1967). Vanadium compounds are poorly absorbed through the gastrointestinal system. Inhalation exposures to vanadium and vanadium compounds result primarily in adverse effects to the respiratory system (Sax, 1984; Ress et al., 2003). Quantitative data are, however, insufficient to derive a subchronic or chronic inhalation reference dose. Other effects have been reported on blood parameters after oral or inhalation exposures (Scibior et al., 2006), on liver (Kobayashi et al., 2006), neurological development in rats (Soaso and Garcia, 2007). Powdered metallic vanadium is a fire hazard, and unless known otherwise, all vanadium compounds should be considered highly toxic. Generally, the higher the oxidation state of vanadium, the more toxic the compound is. The most dangerous compound is vanadium pentoxide. The Occupational Safety and Health Administration (OSHA) has set an exposure limit of $0.05\ mg/m^3$ for vanadium pentoxide dust and $0.1\ mg/m^3$ for vanadium pentoxide fumes in workplace air for an 8-hour workday, 40-hour work week. The National Institute for Occupational Safety and Health (NIOSH) has recommended that $35\ mg/m^3$ of vanadium be considered immediately dangerous to life and health. This is the exposure level of a chemical that is likely to cause permanent health problems or death.

2.5 Vanadium Extraction

The most common vanadium extraction route consists of three process steps; salt roasting and leaching, solution purification and finally precipitation and V_2O_5 fusion. Direct acid and alkali leaching is an alternative to salt roasting. However, they are only used in smaller commercial plants treating U-V ores, catalyst, ash- and boiler-residues which are shown in fig. (2-4) . Commercial extraction of vanadium is feasible in most cases only as a co-product or as by-product to iron in iron –and steelmaking process; which represents 80% of the world □ s present vanadium production. Some vanadium is also produced fom titaniferrous magnetite by direct soda treatment. Oils of the Caribbean and also in some oils from the Middle East contain large quantities of vanadium. Vanadium from these oils is distributed to the market mainly as fly ash and boiler-slag (or boiler-ash). These residues are produced through combustion of oils in electric power plants. The boiler ash is produced directly within the combustion furance while fly ashes are usually collected from the electrostatic precipitators. Another raw material is spent catalysts which are reclaimed both as V-bearing catalyst and as catalyst with deposited vanadium . Vanadium is also produced as a by-product of a few uranium-mining operations on a small scale. [Mikael Lindvall, 2005]

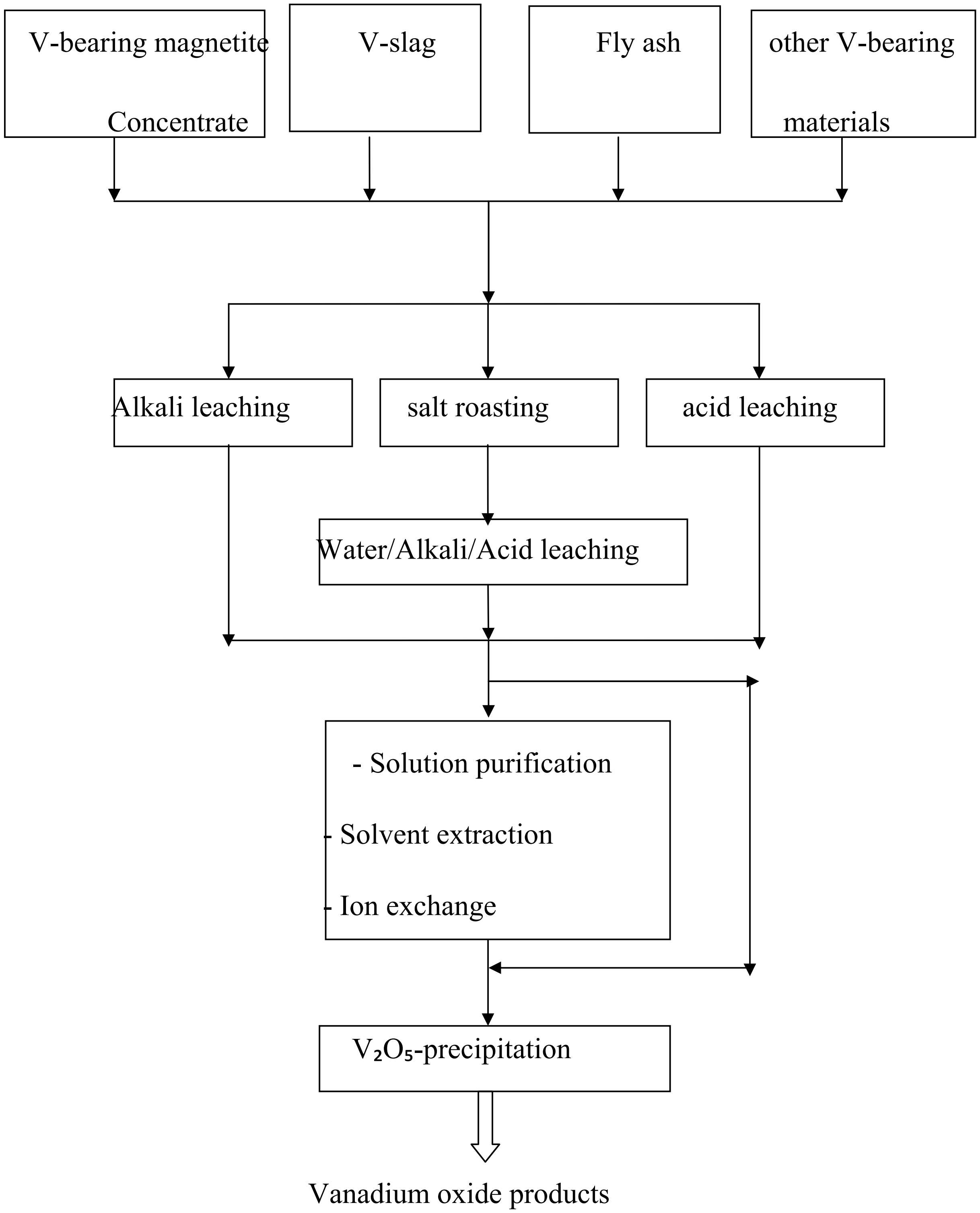

Figure (2-4): Flow sheet of vanadium extraction [C.K Gupta & N.Krishnamurthy, 1992].

- Salt roasting

The objective with salt roasting is to rend the metal-values water soluble; hence an anion its maximum valence state. Soda and sodium sulphate can be used instead of salt; soda roasting and sulphate roasting respectively. The chemical reaction for each regent is summarized in table (2-1). Soda roasting is probably the most used method today due to high environmental requirements. Sodium sulphate is selective but high operational temperature and high price limits its use [C.K Gupta & N.Krishnamurthy, 1992]. Reagents in the table below could be used for the roasting purpose .

Table (2-1) Showstypes of reagents could be used for the roasting purpose [Mikael Lindvall,2005]

Reagents	Chemical reactions	Temperature
NaCl, vapour	$2NaCl+H_2O(g) + V_2O_5 = 2NaVO_3 + 2HCl(g)$	800-900 ℃
NaCl,without varpour	$2NaCl + V_2O_5 = 2NaVO_3 + Cl_2(g)$	
Over roasted	$2NaCl+2NaVO_3+H_2O(g)=Na_4V_2O_7+2HCl(g)$	
Soda	$Na_2CO_3 + V_2O_5 = 2NaVO_3 + CO_2(g)$	900-1200℃
Na_2SO_4	$Na_2SO_4 + V_2O_5 = 2NaVO_3 + SO_3(g)$	1200-1230 ℃

- Leaching and purification

Water is the most commonly used leaching reagent but acid and alkali leaching are also used in some applications. Acid leaching with sulphuric acid ensure that insoluble V- Compounds such as Ca-. Mg- and Fe- vanadates will be solved. Alkali leaching with soda can be used to recover U and V in U-V ores. Soda also solves the insoluble Ca- vanadate. Solution purification is not always necessary but has been used, for example in the processing of titaniferrous magnetite with high chromium content. 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 . Solvent is usually amines

- Vanadium precipitation and V_2O_5 fusion

Water precipitation is the final operation of the V- 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 . Red cake precipitation is one of the more commonly used precipitation processes, as shown in figure (2-5) V_2O_5precipitation from the boiling solution by acidification with sulphuric 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 ; the flow sheet shows two of them . Drying with air or fusion transforms the red cake to products known as technical grade oxide and fused black oxide respectively . Another process for V-recovery in red cake is by ammonium metavanadate crystallization (AMV), producing a product containing 99.9 % V_2O_5.

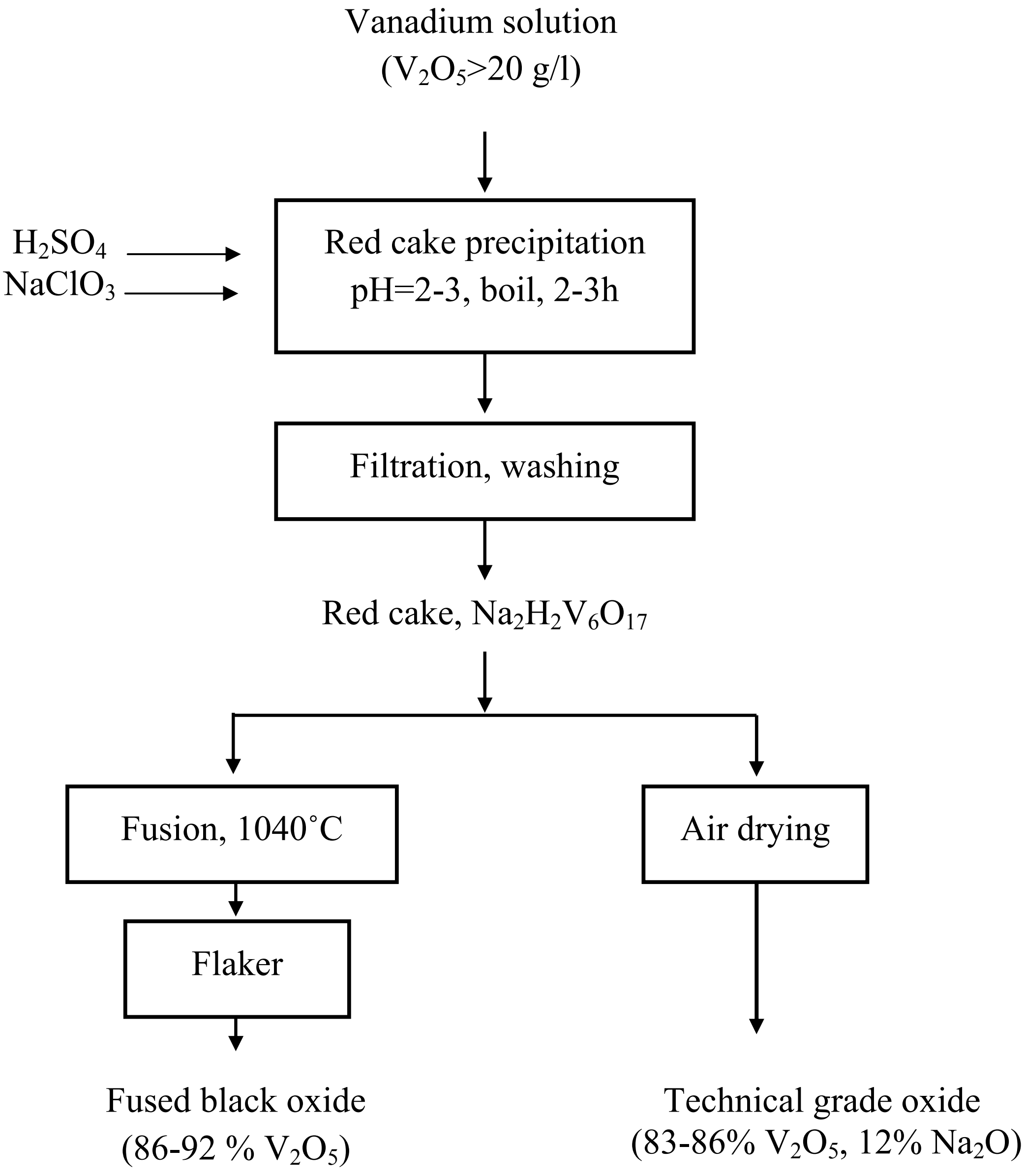

Figure (2-5): Red cake Precipitation. [Mikael Lindvall,2005]

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.

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 number of ways. It can be subdivided in the following fashion:

- **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.

- **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.

- **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 Factors influencing the rate of extraction [Richardson et al. , 2002]

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

- **Particle size**

  Particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid . 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 particles from the liquid and drainage of the solid residue are made more difficult. It is generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction and, in particular, the production of a large amount of fine material should be avoided as this may wedge in the interstices of the larger particles and impede the flow of the solvent.

- **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, although as 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.

- **Temperature**

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

- **Agitation of the fluid**

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

- **Leaching Time**

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

2.8 Leaching [Richardson et al. , 2002]

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 . Leaching is concerned with the extraction of a soluble constituent from a solid by means of a solvent. The process may be used either for the production of a concentrated solution of a valuable solid material, or in order to remove an insoluble solid, such as a pigment, from a soluble material with which it is contaminated. The method used for the extraction is determined by the proportion of soluble constituent present, its distribution throughout the solid, the nature of the solid and the particle size. If the solute is uniformly dispersed in the solid, the material near the surface will be dissolved first, leaving a porous structure in the solid residue. The solvent will then have to penetrate this outer layer before it can reach further solute, and the process will become progressively more difficult and the extraction rate will fall. If the solute forms a very high proportion of the solid, the porous structure may break down almost immediately to give a fine deposit of insoluble residue, and access of solvent to the solute will not be impeded. Generally, the process can be considered in three parts: first the change of phase of the solute as it dissolves in the solvent, secondly its diffusion through the solvent in the pores of the solid to the outside of the particle, and thirdly the transfer of the solute from the solution in contact with the particles to the main bulk of the solution. Any one of these three processes may be responsible for limiting the extraction rate, though the first process usually occurs so rapidly that it has a negligible effect on the overall rate.

The reactions between solid compounds and liquid phases are heterogeneous processes. The reaction rate may be controlled either by mass transfer to and from the solid surface or by the chemical reaction on the surface, as well as by combinations of two steps. In the first case the rate of dissolution is increased by stirring of the liquid. In the second case the rate is independent of the motion of the liquid. In both cases the rate will increase with increasing concentration of the reaction components in the solvent. Also mass transfer to and from the surface has a lower activation energy than the chemical reaction, and will be controlling at higher temperatures [Robins, 1967].

2.9 Recovery of Vanadium

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 . Tamlin and Smith [2007].

Vanadium recovery from clay vanadium mineral using an acid leaching method studied by Haoran et al. [2007] by using an acid leaching method . A technique including direct acid leaching, vanadium precipitation with alkaline, sodium hydroxide releaching, impurity removing by adjusting pH value, precipitation vanadium with ammonium chloride, and vanadium pentoxide by roasting steps was proposed according to the characteristic of Xichuan clay vanadium mineral. The factors influencing leaching vanadium such as temperature and the concentration of sulfuric acid were investigated and optimized. The experimental results indicated that the extract ratios of V_2O_5 can reach 94% and 92% at a sodium chlorate ratio of 3% and a manganese dioxide ratio of 3%, respectively. A completely chemical precipitation method was adopted to decontaminate and enrich the vanadium in the acid leaching solution. Analysis of vanadium pentoxide indicates that the purity of final vanadium pent oxide can reach 99% and meet the standard specifications. The total recovery can reach about 75%. The technique has the characteristics of simplicity, less investment, and more environment safety as compared with the traditional salt roasting method.

Recovery of vanadium, nickel and molybdenum from fly ash of heavy oil-fired electrical power station studied by Stas et al. [2006] by Two stage , A first stage was an alkaline leaching of fly ash to recover vanadium and molybdenum followed by a second stage using sulfuric acid leaching of the residual ash to recover nickel. The yield of vanadium recovery was more than 90% while nickel recovery was 80%. Preparatory tests were performed to establish the best leaching operational parameters (Temperature, mixing time, liquid(mL)/solid(g) ratio (L/S), and sodium hydroxide concentration), the best operating conditions for first stage to obtain high yield of V recovery and good concentration of V in the leach liquor is: (NaOH = 8M, L/S = 5, T = 100 ℃, mixing time = 3h). A block diagram for recovery of vanadium and molybdenum from fly ash is given in Fig.(2.6).

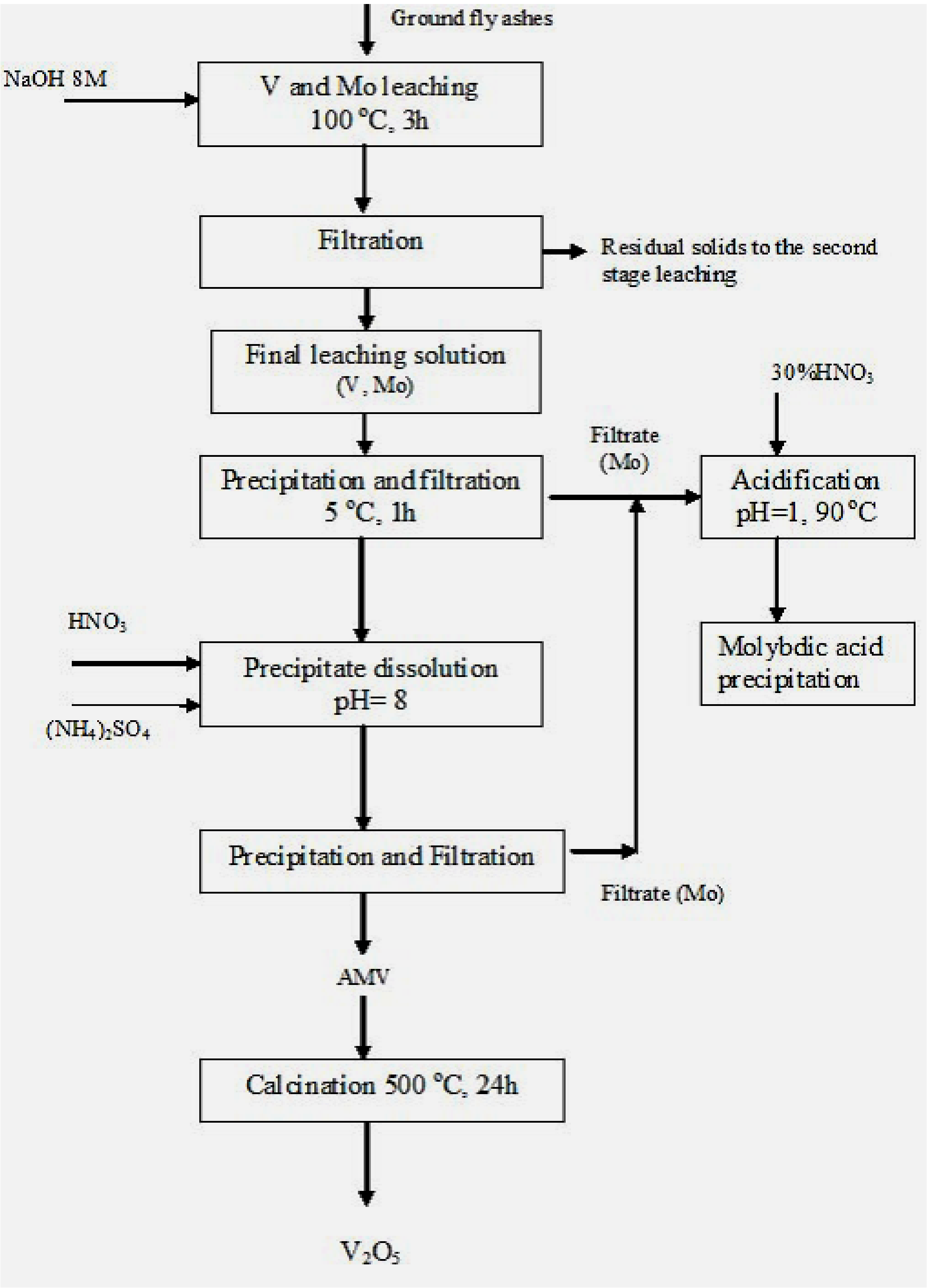

Figure (2-6): First stage leaching to recover V and Mo Recovery of V, Ni and molybdenum from fly ash of heavy oil-fired electrical power station [Stas et al., 2006] .

The best operating conditions for second stage to obtain 80% of nickel recovery are: ($H2SO4$ = 5 M, T = 100℃ , t = 3 h, L/S = 4). A block diagram for recovery of Ni from the residual ashes is given in Fig.(2-7).

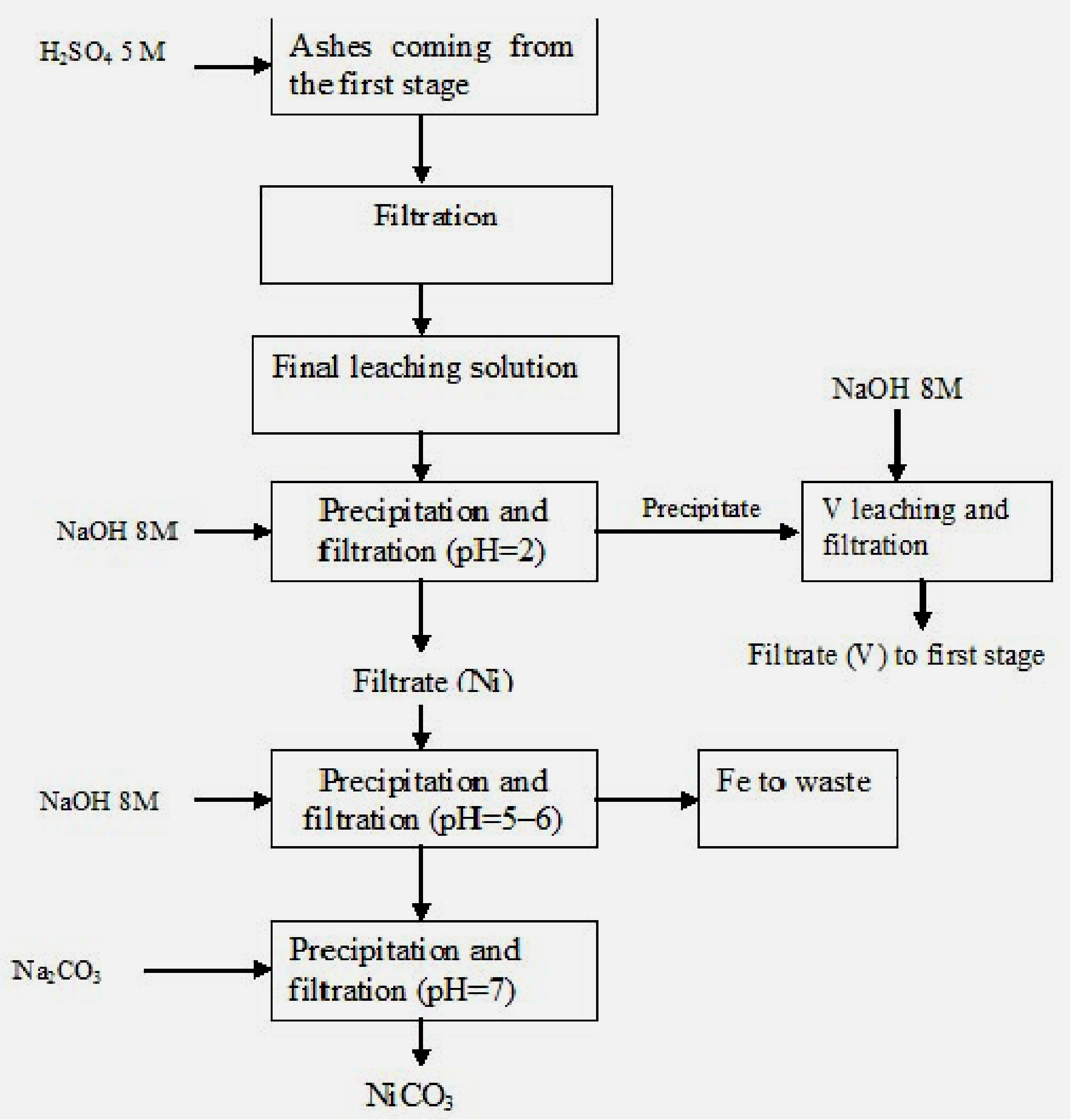

Figure (2-7): Second stage leaching to recover nickel
Recovery of V, Ni and molybdenum from fly ash of heavy oil-fired electrical power station [Stas et al., 2006]

A comparative study of the solvent extraction of vanadium in sulphate media using primary amine PRIMENE 81R and tertiary amine ALAMINE 336 dissolved in kerosene has been carried out by Lozano، and Godínez [2002]. mechanism proposal an extraction isotherms have been determined, pH conditions for both amines, yielding best results for primary amine. Equilibrium studies were used to assess the conditions of vanadium recovery in a continuous counter-current process using leaching solutions.

Recovery of vanadium pentoxide from spent sulphuric acid catalysts studied by S. Khorfa et al. [2002] ,using a three-step process involving acid leaching, oxidation and precipitation. Several different acids were used in the leaching, sulphuric acid was used in various concentrations, solid to liquid ratios, stirring times and temperatures. A high solid/liquid ratio in the leaching stage was used to obtain high concentration of vanadium pent oxide and low acid consumption that allowed direct precipitation without the use of extraction by rather expensive organic solvents. Sodium carbonate solution of one mole/liter concentration was used in the precipitation stage. Sulphuric acid was found to be the best leaching solution. The efficiency of recovery decreases by increasing the concentration of the acid. Leaching efficiency of 96.6% was achieved and the concentration of vanadium in the spent catalyst was tested to be 0.187%. It is not toxic and by adding it to the second leaching stage it is possible to reduce the concentration of vanadium in the waste. The efficiency of the precipitation process was 73% and the concentration of vanadium in the filtrate was 0.19%, it is not toxic either. Vanadium pentoxide can be recovered from the initial spent catalytic mass with an overall efficiency of 70%.

Recovery of Vanadium from Fly Ash and Spent Catalysts, Studied by G.V.K. Puvvada et al. [2002], the results of their investigations for the recovery of vanadium from spent catalysts and fly ash obtained from processing tar sands. Processes used included flotation, leaching and finally ion exchange. They also described the recovery of vanadium from spent catalysts, which was attempted through sulphidizing roasting followed by acid leaching.

The recovery of vanadium from heavy oil fly ash having a high carbon content was performed by Sandra Vitolo et al. [2001] using a four-step process consisting of a preliminary burning in order to reduce the carbonaceous fraction, followed by an acid leaching and an oxidative precipitation of vanadium pentoxide. The preliminary burning was conducted in the temperature range 650 to 1150 °C, below the initial deformation temperature (IDT) of the fly ash. The temperature of the preliminary burning step was revealed to be a significant parameter. Above 950 °C various phenomena (fusion, volatilisation of V, formation of V–Ni refractory compounds) occurred that adversely affected the recovery of vanadium. The burning temperature of 850 °C was found to be the best as a result of the trade-off between the overall vanadium recovery yield (83%) and the V_2O_5 weight percentage in the precipitate (84.8%).

Lozano and Juan [2001] studied the recovery of vanadium contained in spent catalysts from the manufacture of sulphric acid, they found that the variables influencing the leaching process are: leaching agent concentration, (Solid/Liquid) ratio, stirring speed and temperature, allowed more advantageous industrial conditions to be determined and verified that the process is diffusion controlled. The work was completed by developing an industrial leaching cycle simulation with the aim of reproducing the real performance of spent catalyst, proposed operating conditions, and verifying that the final residue obtained was not toxic.

Luis and Cury [2000] Studied Vanadium recovery by leaching in Spent Catalysts for Sulfuric Acid Production. The factor effect on process is particle size, temperature, acid concentration and agitation intensity. Results showed strong dependency between remaining vanadium content and particle size. Temperature has shown lesser influence,the spent sulfuric acid production catalysts can be leached with sulfuric acid to reduce its vanadium content so that they can safely be disposed as inert materials. Leaching velocity showed to be influenced by particle dimensions and temperature and does not depend on the sulfuric acid concentration nor agitation speed. This result indicates that the dominant resistance of the process is the intra-particle diffusion. The Vanadium content showed no significant variation after 6 cycles so that steady state conditions were achieved. The match between predicted and observed values allowed the proposal of a flowsheet of the process as seen in fig.(2-8) and the list of equipments shows in table 2-2 .

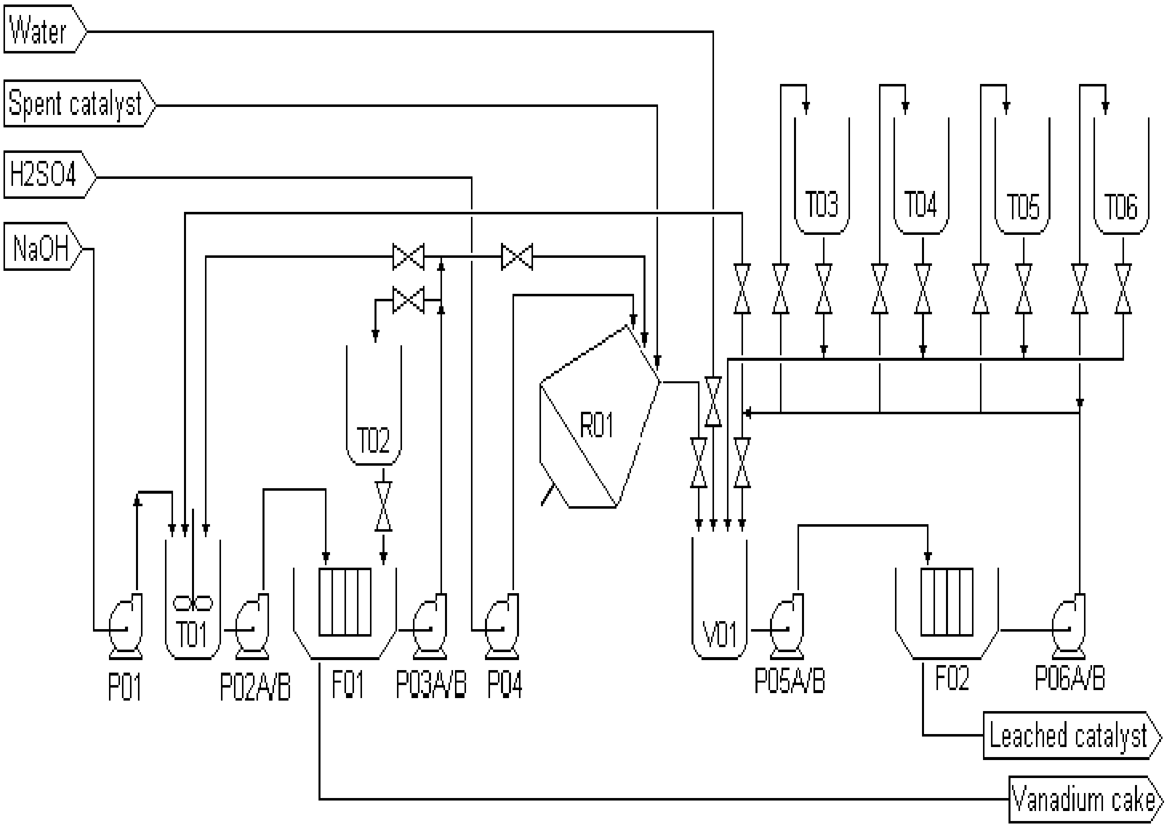

Figure (2-8): Flow sheet of the process of vanadium recovery by leaching in spent catalyst for Sulfuric Acid Production [Jose Luis and George Cury,2000]

Table (2-2): EQUIPMENTS LIST [Jose Luis and George Cury, 2000]

Item	Tag	Description
1	B01	Sump pump, PVC or poliethylene
2	B02A/B	Centrifugal pump, 5 m3/h, poliethylene
3	B03A/B	Centrifugal pump, 5 m3/h, poliethylene
4	B04	Sump pump, PVC or poliethylene
5	B05A/B	Centrifugal pump, 3 m3/h, poliethylene
6	B06A/B	Centrifugal pump, 3 m3/h, poliethylene
7	BT01	Rotary reactor, 1m3, phenolic resin linned carbon steel
8	C01	Discharge vessel, 1m3, phenolic resin linned carbon steel
9	FP01	Press filter, 12 m2, poliethylene
10	FP02	Press filter, 3 m2, poliethylene
11	TQ01	Agiteted vessel, 3m3, phenolic resin linned carbon steel
12	TQ02	Agiteted vessel, 3m3, phenolic resin linned carbon steel
13	TQ3/4/5/6	Agiteted vessel, 0.35m3, phenolic resin linned carbon steel

Recovery of vanadium from heavy oil and Orimulsion fly ashes studiedby Sandra Vitolo et al. [2000]This work concerns a three-step process for the recovery of vanadium from heavy oil and Orimulsion combustion fly ashes. This consisted of acid leaching, oxidation and precipitation of the vanadium pentoxide, followed by washing of the precipitate. Preliminary tests were conducted to investigate the effect of some operating parameters for the various steps of the process. After these preliminary tests, the recovery of vanadium from the fly ash samples was performed on a laboratory scale and the overall yield of the process was determined. By washing the precipitate, it was possible to reduce the concentration of the impurities and to allow its use for the production of ferrovanadium alloys.

The conventional method for recovering vanadium from vanadium containing ores was studied by Hansen [1987]. This method included 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 was then cooled, crushed, ground and water leached in agitation leach tank in a conventional manner. The solubilized sodium vanadate in solution was recovered from the solids through convential solid-liquid separation such as filtration or counter current decantation.

The latter step generally involved precipitating the vanadium as ammonium metavanadate. In some instances, the filtrate was evaporated after precipitation to recover the sodium salt and to avoid liquid effluent disposal. Recovery methods are sought which not only enable a high percentage of recovered vanadium but also provide a high grade of leach liquor. A heap leaching process was proposed for recovery of various metal values from ores. In the heap leaching process, the ore was placed in a pale and the leaching liquor was placed on top of ore and then seeped through the depth of the pile where by metal values were dissolved in the liquor and the liquor was recovered at the bottom of the pile and treated to recover the metal values. This process was conducted to recover at least 75 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 was often about 50-500 liters per square meter per day. Generally, the leaching solution had a pH of at least about 7.

It was reported in 1966 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 alkayl 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 the red cake, and converted to 98% V_2O_5 by heating [Merrit, 1971].The flow sheet for the plant is shown in figure (2-9).

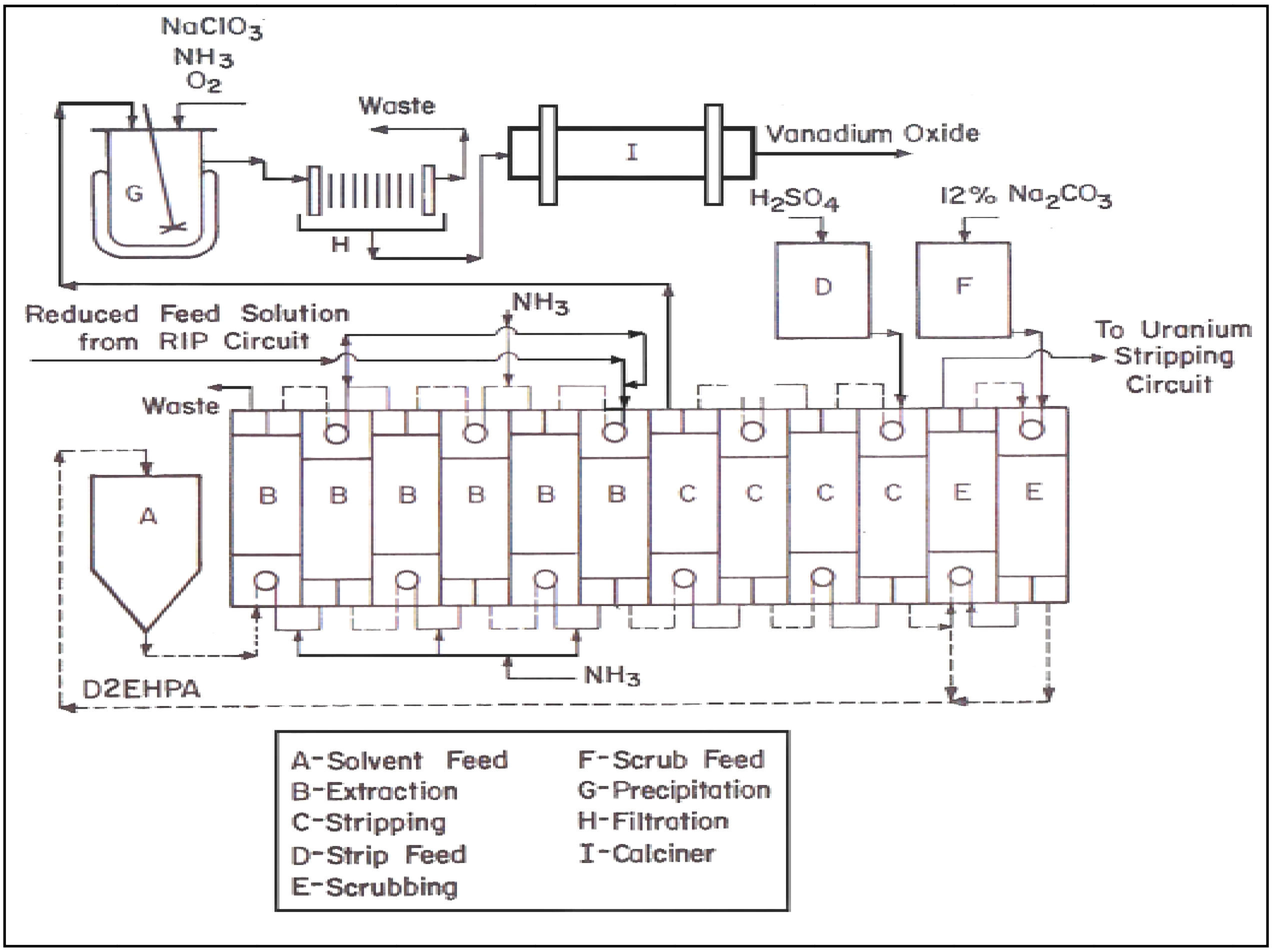

Figure (2-9): Flow sheet for the plant of extraction in mixer settler for Vanadium recovery [Merrit, 1971].

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.

Vanadium corporation of America, Durango, Colorado, operated with a mixed solvent 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, was resulted from the water leach of a salt-roast product. The solution was oxidized with potassium permanganate before extraction. The result of the mixed extracting 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].

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} cat ions can be extracted from chloride solutions containing 0.01-1.0 mol/dm^3 acid by D2EHPA in kerosene. 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} cat ion can 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.

The content of vanadium in Iraqi crude oil is associated with it density , being of the order of 200 ppm in the heavey Gayyarra oil and about 30 ppm in the lighter more economically important oil.The fuel oil used in electric power stations releases ash, which contains 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 100-120ppm vanadium when heavy fuel 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].

In Iraq there are many researchers who studied the recovery of vanadium like Jassim [1998] who used a solvent extraction technique as a separation method to separate a vanadium from the leach solution of the ashes of burned fuel oil at Electrical Power Station in Iraq. Tributyl phosphate (TBP) was used as an extracting agent through mixer-settler batteries. Some Parameteres, which influenced vanadium extraction , were studied in detail, such as chloride ion concentration and the acidity of the mother solution , in addition to the number of extraction , stripping stage and phase ratios.A pilot plant has been designed and installed at Ibn Cina company site Tarmiya, for the recovery of vanadium from scale and ash residues of some Iraqi oil- fired power stations as shown in figure (2-10). The plant utilizes the following processes [Jassim,1998] :

1- Leaching with NaOH solutions at about 95℃, according to the following equation: $V_2O_5 + 2NaOH \rightarrow 2\ NaVO_3 + H_2O$
2- Filtration of the leach solution .
3- Precipitation of ammonium meta-vanadate, NH_4VO_3 using ammonia solution.
4- Calaination of ammonium vanadium is presence of oxygen to produce vanadium pentoxide.

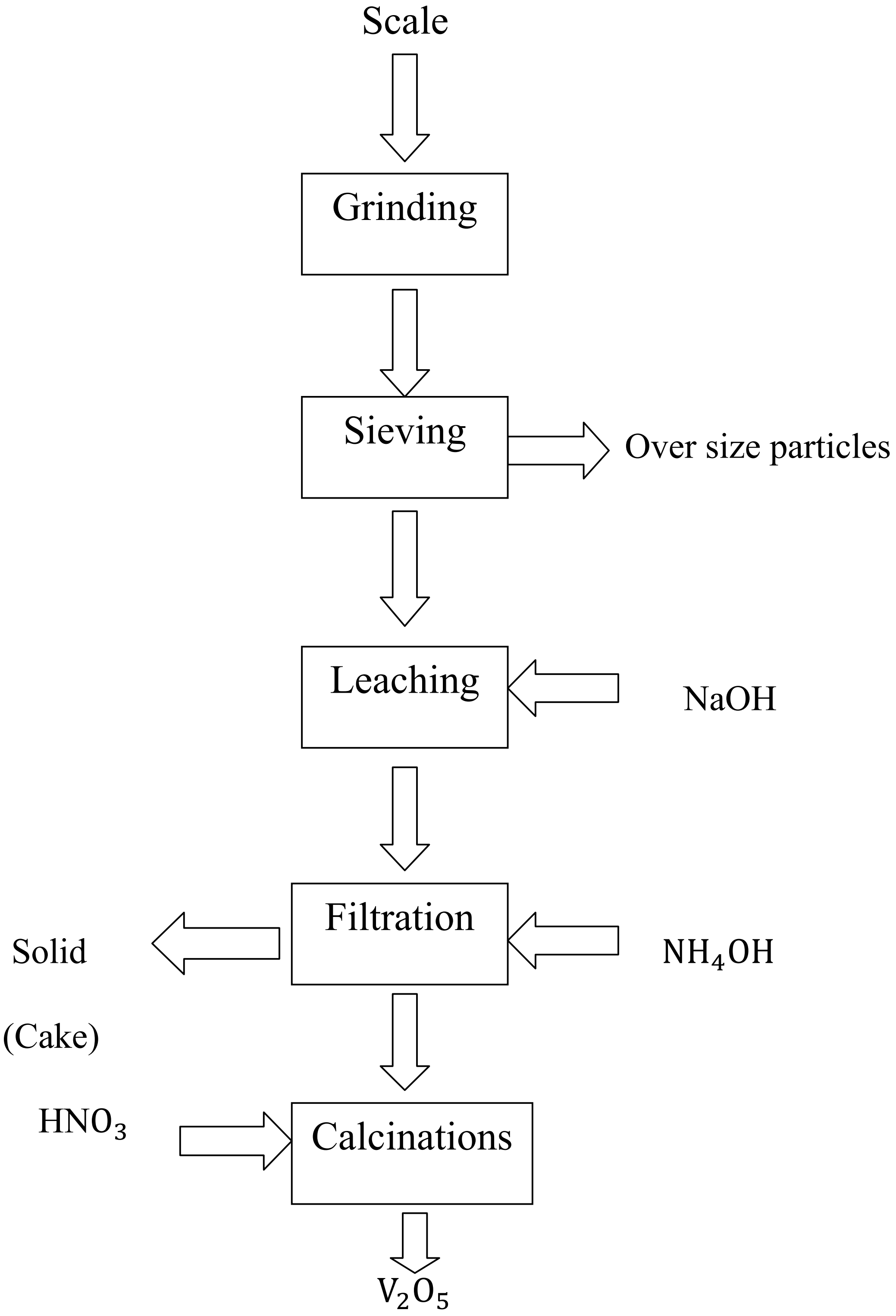

Figure (2-10): Block Diagram of Vanadium recovery by Alkalin in Ibn Cina.

[Jassim, 1998]

Al-Zobai [1999] recovered vanadium from scale residues of oil-fired power stations by alkaline leaching method using sodium hydroxide solution . 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

$$V_2O_5 + 2NaOH \rightarrow 2NaVO_3 + H_2O$$

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

$$NaVO_3 + NH_4OH \rightarrow 2NH_4VO_3 + NaOH$$

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

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

The effects of process available by temperature, 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: Increasing temperature, Decreasing dp, Increasing molarities of NaOH and Increasing leaching time. A complete vanadium conversion was achieved at (373 K, 125 μm, 3 hr), And (373 K , 150 μm, 4 h,4M).

M.Jalhoom et al. [2001] studied Separation of Vanadium Trioxide from the Residue of heavey oil. Vanadium Trioxide (V_2O_3) was prepared from vanadium pentoxide (V_2O_5) which was extracted from residue of oil fired fly ash in power plant by using hydrogen gas as reducing agent, (V_2O_3) reduction was performed inside an evacuated system, designed by the authors. The optimized reduction conditions were temperature 500 ˚C, flow rate of hydrogen gas 0.5 liter/min. , time 3 hr, to obtain (V_2O_3) of purity around 98%.

M.Jalhoom et al. [2007] recovered vanadium through extraction process of nickel metal from residual of fired heavy oil in electric power station by Hydrometallurgy method. The residual was retreatment by grinding and sieving, and the nickel was concentrated by particle size. Magnetic separation was also performed in order to get rid of iron that was in heavy oil residual in the form of magnetite, and the results showed the ability of separating 86% of iron. Vanadium was recovered from the residual by alkaline leaching method using sodium hydroxide solution and this step resulted in the leaching 98.63% of vanadium, also increasing nickel concentration to 16.27%.

Al-Bayati [2008] studied the kinetics of vanadium recovery from scale residues of oil-fired power stations by alkaline leaching method using sodium hydroxide solution where Vanadium conversion increase when temperature increases, particle size decreases, time increase. A second order polynomial mathematical correlation was employed in the range of independent variables temperature (60-100)˚C, particle size (125-200) µm, time up to 8 h with correction of 0.9990 . The diffusion through ash layer is the controlling step which has the highest resistance among other steps , A complete vanadium conversion was achieved at (373 K, 150 μm, 7 h), And (373 K , 150 μm, 5 h).

3.1 Heterogeneous reactions [Richardson and Harker, 2002]

Heterogeneous reactions occur between all combinations of gas, liquid, and solid phases. The solids may be inert or reactive or catalysts in granular form. Reactants migrate between phases in order to react: from gas phase to liquid, from fluid to solid, and between liquids when the reaction occurs in both phases. One of the liquids usually is aqueous.

3.1.1 Factors Affecting Heterogeneous Reactions [Richardson and Harker, 2002]

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.

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

3.2.1 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 un-catalyzed heterogeneous system can he considered to take place in series and/or in parallel. Hence the overall rate expression may be formulated by combining terms for the various process steps involved.

This type of reaction may consists of the following steps

1- 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.

2- Diffusion of reactants from the interface to the bulk of the second phase.

3- Chemical reaction between the reactants from phase one and those in phase two.

4- 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 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.

3.3 Reaction Models [Perry et al., 1997, Smith, 1981 and Levenspiel, 1999]

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:

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

The requirement for a good engineering model is that it be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with it. Unfortunately, in today's age of computers, this all too often happens. For the noncatalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the progressive-conversion model and the shrinking unreacted-core model.

3.3.1 Progressive-conversion Model

Progressive-Conversion Model (PCM). Can be visualized that reactant liquid Enters and reacts throughout the particle at all times, most likely at different Rates at different locations within the particle. Thus, solid reactant is converted Continuously and progressively throughout the particle as shown in Fig. 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.

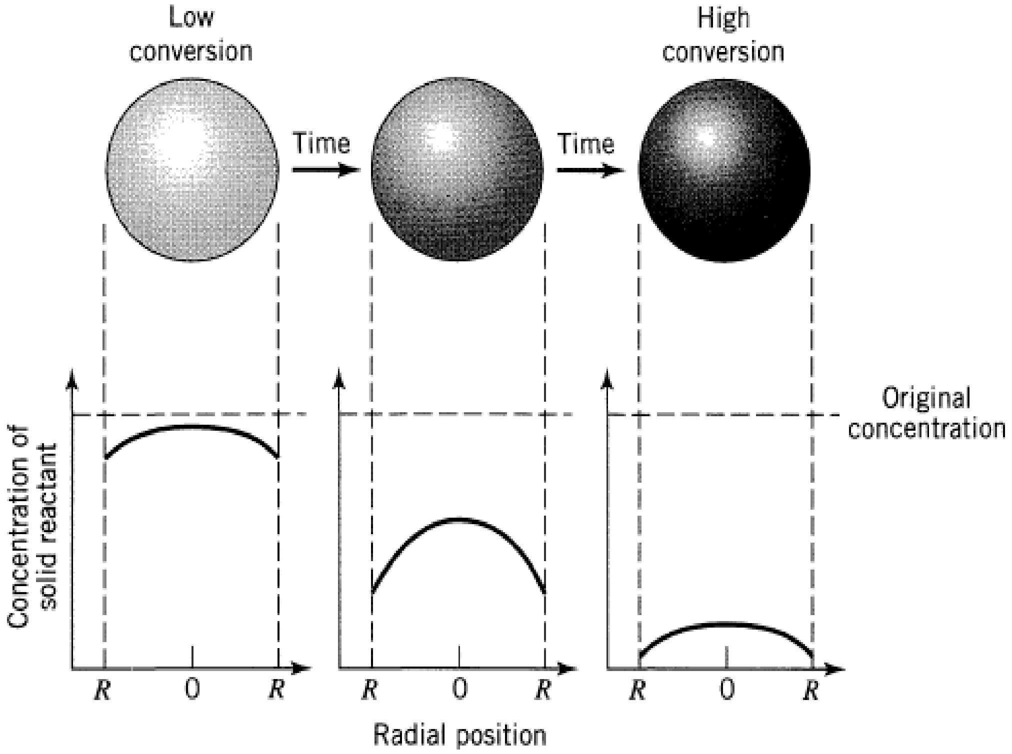

Fig. 3-1 Progressive-conversion model [Levenspiel, 1999]

3.3.2 Unreacted-core Shrinking Model

Shrinking-Core Model (SCM). Can be visualized that reaction occurs 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. We refer to these as "ash." Thus, at any time there exists an unreacted core of material which shrinks in size during reaction, as shown in Fig. 3-2

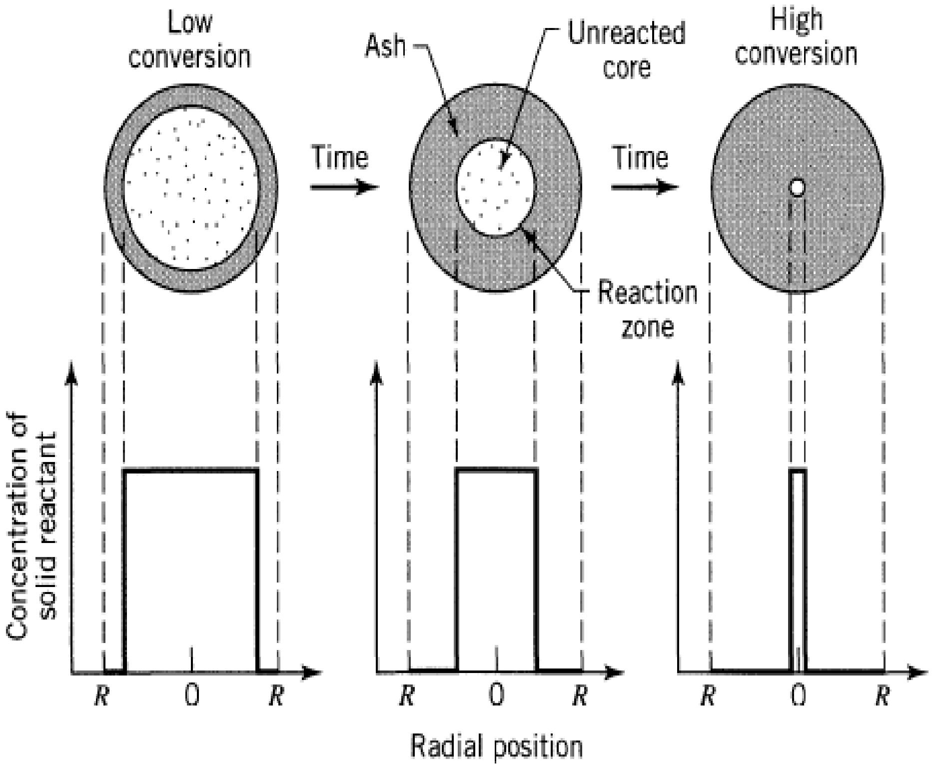

Fig. 3-2 Steps of unreacted-core shrinking model [Levenspiel, 1999]

3.3.3 Unreacted-core Model for Spherical Particles of Unchanged Size

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 fluid 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 fluid A with solid at this reaction surface.

Step 4. Diffusion of fluid poducts through the ash back to the exterior surface of the solid.

Step 5. Diffusion of fluid 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.

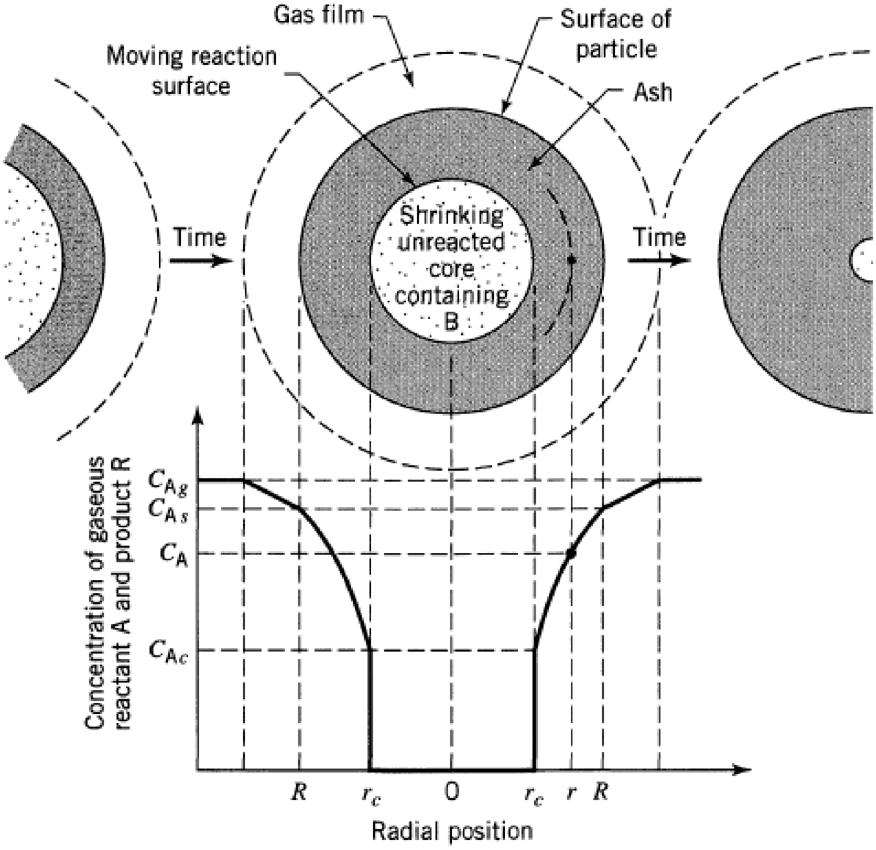

Fig. 3-3 Schematic diagram of concentration profile for the unreacted-core shrinking model [Levenspiel, 1999]

3.3.3.1 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.

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

Where $bk_g(C_{A0}-C_{AS}) = bk_g C_{A0}$ = Constant

$$N_B=\rho_B V \qquad \ldots(3.3)$$

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:

$$-dN_B=-bdN_A=-\rho_B dV=-\rho_B d\left(\frac{4}{3}\pi r_c^3\right)=-4\pi\rho_B r_c^2 dr_c \qquad \ldots(3.4)$$

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

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt}=-\frac{\rho_B r_c^2}{R^2}\frac{dr_c}{dt}=bk_g C_{Ao} \qquad \ldots(3.5)$$

By integration:

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

From Equation 3.6, at complete reaction;

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

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;

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

3.3.3.2 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:

$$-\ \frac{\mathrm{dN_B}}{\mathrm{dt}} = 4\pi r^2 \mathcal{Q} = 4\pi R^2 \mathcal{Q}_{\mathrm{As}} = 4\pi r^2 \mathcal{Q}_{\mathrm{Ao}} = \text{constant} \qquad \ldots(3.11)$$

$$\mathcal{Q}A = \mathcal{D}e\ \frac{\mathrm{dC_{A0}}}{\mathrm{dr}} \qquad \ldots(3.12)$$

Combining Equation 3.11 and 3.12 gives;

$$-\ \frac{\mathrm{dN_B}}{\mathrm{dt}} = 4\pi r^2 \mathcal{D}e\ \frac{\mathrm{dC_{A0}}}{\mathrm{dr}} = \text{constant} \qquad \ldots(3.13)$$

Integration Equation 3.13 gives;

$$-\ \frac{\mathrm{dN_B}}{\mathrm{dt}} = \left(\frac{1}{r_c} - \frac{1}{R}\right) = 4\pi\ \mathcal{D}e\ \mathrm{C_{A0}} \qquad \ldots(3.14)$$

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;

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

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

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

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

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

3.3.3.3 Chemical Reaction Controls

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

$$-\frac{1}{4\pi r_c^2}\frac{dN_B}{dt} = -\frac{b}{4\pi r_c^2}\frac{dN_A}{dt} = bkC_{Ao} \qquad \ldots(3.19)$$

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

$$-\frac{1}{4\pi r_c^2}\rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B\frac{dr_c}{dt} = bkC_{Ao} \qquad \ldots(3.20)$$

Or;

$$t = \frac{\rho_B}{bkC_{Ao}}\left(R - r_c\right) \qquad \ldots(3.21)$$

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

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

Combining Equations 3.21 and 3.22 gives;

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

Table 3-1: Shows comparison of the different Controlling steps in the Fluid-Solid Reaction for Sphere Particle [Levenspiel, 1999].

	Fluid film	Ash layer	Chemical Reaction
T	$\frac{\rho_B R}{3bk_g C_A}$	$\frac{\rho_B R^2}{6b \mathcal{D}ek_g C_A}$	$\frac{\rho_B R}{bk_g C_A}$
t/τ	X_B	$1-3(1 - X_B)^{2/3}+2(1 - X_B)$	$1-(1 - X_B)^{1/3}$

3.4 Determination of the rate –controlling step [Levenspiel, 1999]

The kinetics and rate-controlling steps of a fluid-solid reaction are 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 aguide to experimentation and to the interpretation of experimental data.

3.4.1 Temperature

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

3.4.2 Time

Figure 3.4 shows the progressive conversion of spherical solids When chemical reaction, film diffusion, and ash diffusion in turn control. Results Of kinetic runs compared with these predicted curves should indicate the rate controlling step. Unfortunately, the difference between ash diffusion and chemical reaction as controlling steps is not great and may be masked by the scatter in experimental data.

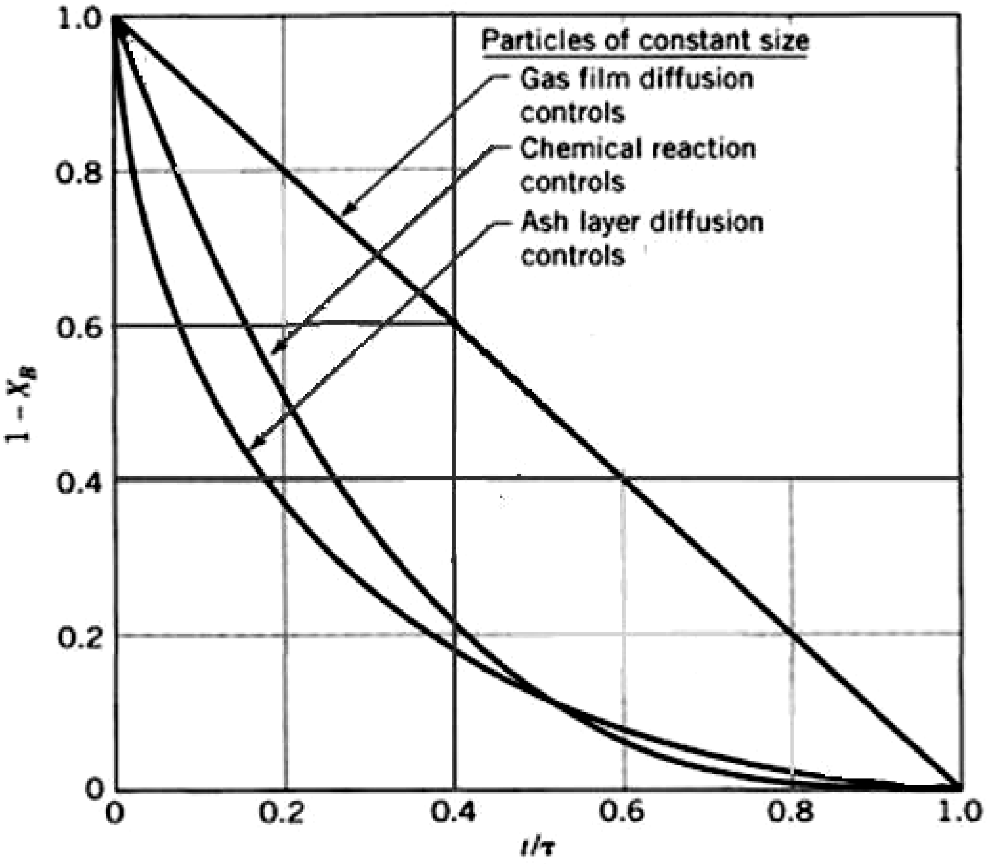

Figure 3-4 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion. [Levenspiel, 1999]

4.1 Materials

4.1.1 Sodium Hydroxide

Sodium hydroxide (manufactured in Saudi Arabia) was used as leaching solution. The molecular weight of Sodium hydroxide is 40.00-gm/gmole and melting point (318.4ºC).

Appropriate quantities of solid NaOH were dissolved in water to make up the required molarities (2-4) molar which were used in the present work.

Table 4-1 Shows Physical Properties of NaOH

Compound (Formula)	Mol.Wt	Specific Gravity	Melting Point	Boiling Point	Solubility in Water
Sodium Hydroxide (NaOH)	40	2.13	318.4	1390	42 (0˚C)

4.1.2 Spent catalyst

Spent catalyst used in the manufacture of sulfuric acid by **Contact Process** that involving the catalytic oxidation of sulfur dioxide, SO_2, to sulfur trioxide, SO_3.

$$2SO_2\,(g) + O_2\,(g) \text{----->} 2SO_3\,(g)$$

Spent catalyst taken from (Al-Sadra company for limited cleaning materials production in the west of Baghdad), Solid samples of the powder stock, which was used in this work were analyzed for vanadium content by means of Atomic Adsorption spectrometry at the analytical laboratory of Ibn Cina Company, Appropriate quantities of solid samples taken and dissolved in (aulic water) containing solution of (3 HCl +1HNO_3), the average percentage was found to be (37 %). This value was used in the calculation of vanadium recovery for each experiment.

Table 4-2 Shows Physical Properties of V_2O_5

Compound (Formula)	Mol.Wt	Specific Gravity	Melting Point	Boiling Point	Solubility in Water
Vanadium Pentoxide (V_2O_5)	181.9	3.357	800	1750	0.8 (20˚C)

4.2 Laboratory experimental unit

Experiments were carried out in (1 litter) glass reactor, the diameter of glass reactor was 12cm and the height was 10 cm applying on heating mantle with controller of temperature , and a mixer consisted of stainless steel shaft , screwed with four pitched turbine blades impeller , the diameter of impeller was 4 cm. The stirrer rotated by means of an electrical motor coupled to achieve 600 rpm, The mixer was screwed with stand and two hands to infixing mixer and thermometer. The motor of mixer and heating mantle was connected to controller of electricity.

- **Thermometer**

Temperature of the reaction was measured by means of calibrated mercury in glass thermometer with range 0-250 ºC.

- **Heating mantle**

Heating mantle was used for heating the solution to the required temperature (60 to 100 ºC).

- **Impeller**

Stainless steel stirrer with pitched blade turbine blades was used for mixing. The stirrer rotated by means of an electrical motor coupled to achieve 600 rpm.

A schematic diagram of the equipment is show in figure (4-1).

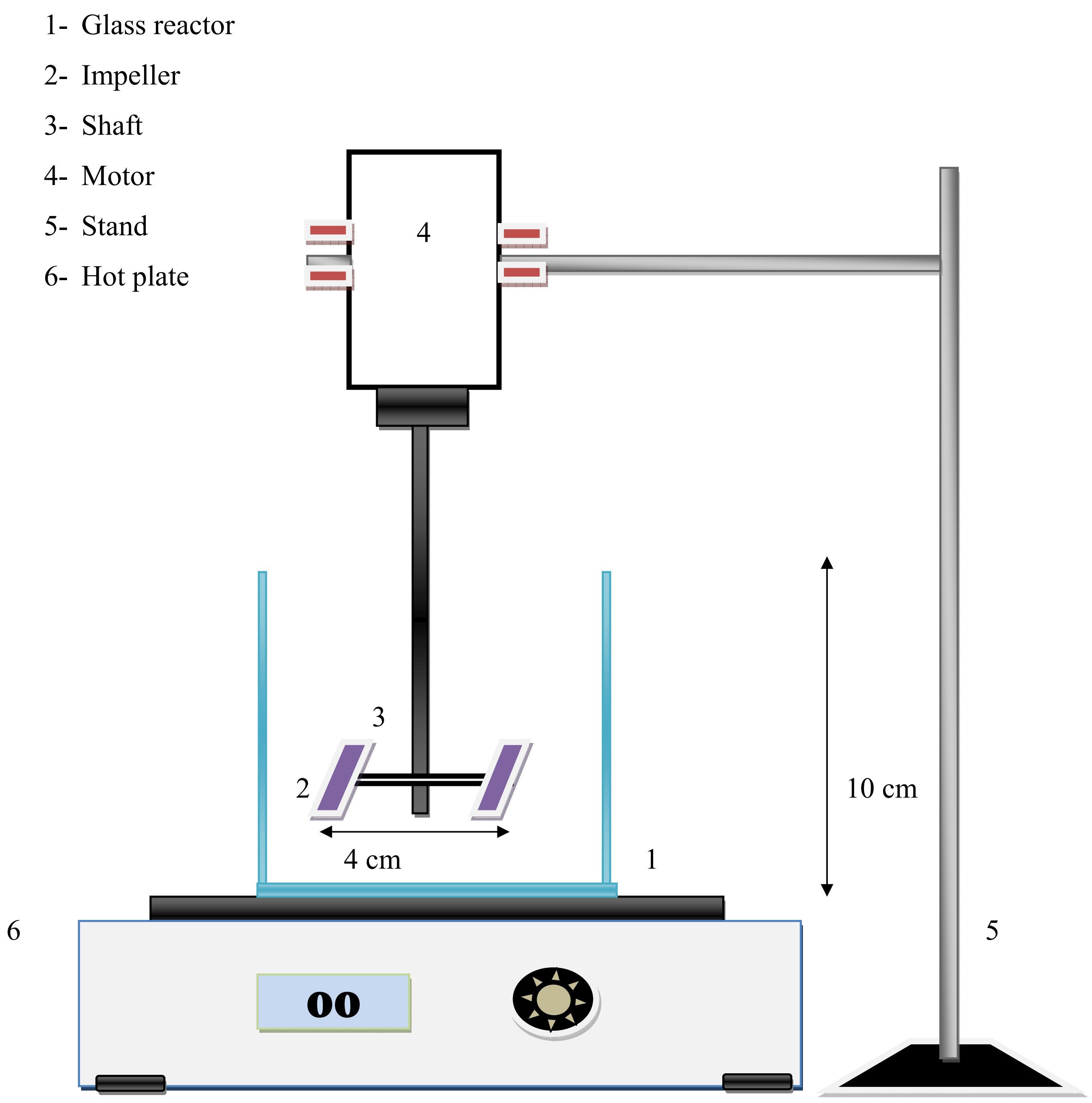

Fig. (4-1) A schematic Diagram of the leaching set-up

4.3 Experimental procedure

The sample of spent catalyst, used in this experimental work was a solid material taken randomly, grinded and sieved by means of laboratory sieve to obtain particle by adding size (100-200µm).

The required (2-4) molar solution of sodium hydroxide was calculates as follows experimental tank.
The solution was then heated to the desired temperature (60-100ºC) during stirring at 600 rpm. 100 gm of spent catalyst with particle size in the rang (100 -200µm) was added to the aqueous solution of sodium hydroxide. During the leaching process, the following reaction is occurred

$$V_2O_5 + 2\,NaOH \rightarrow 2\,NaVO_3 + H_2O$$

After the desired time (1-5 hr) the solution was filtered to remove the unreacted vanadium and impurities. A fixed volume of 500 ml was assured throughout all experiments. For the experiments at high temperature 80-100℃ , it was necessary to make up the volume correction by adding an amount of water to compensate for the evaporation during the specified times of experiments. The block diagram of figure (4-2) shows the processes.

Samples of solutions from all experiments were analyzed for vanadium by means of Atomic Adsorption at the analytical laboratory of Ibn Cina Company.

Name: Atomic Adsorption Flame Emission Spectrophotometer

Model: AA680

Type: (Shimadzu)

Length: 314.4 Nm

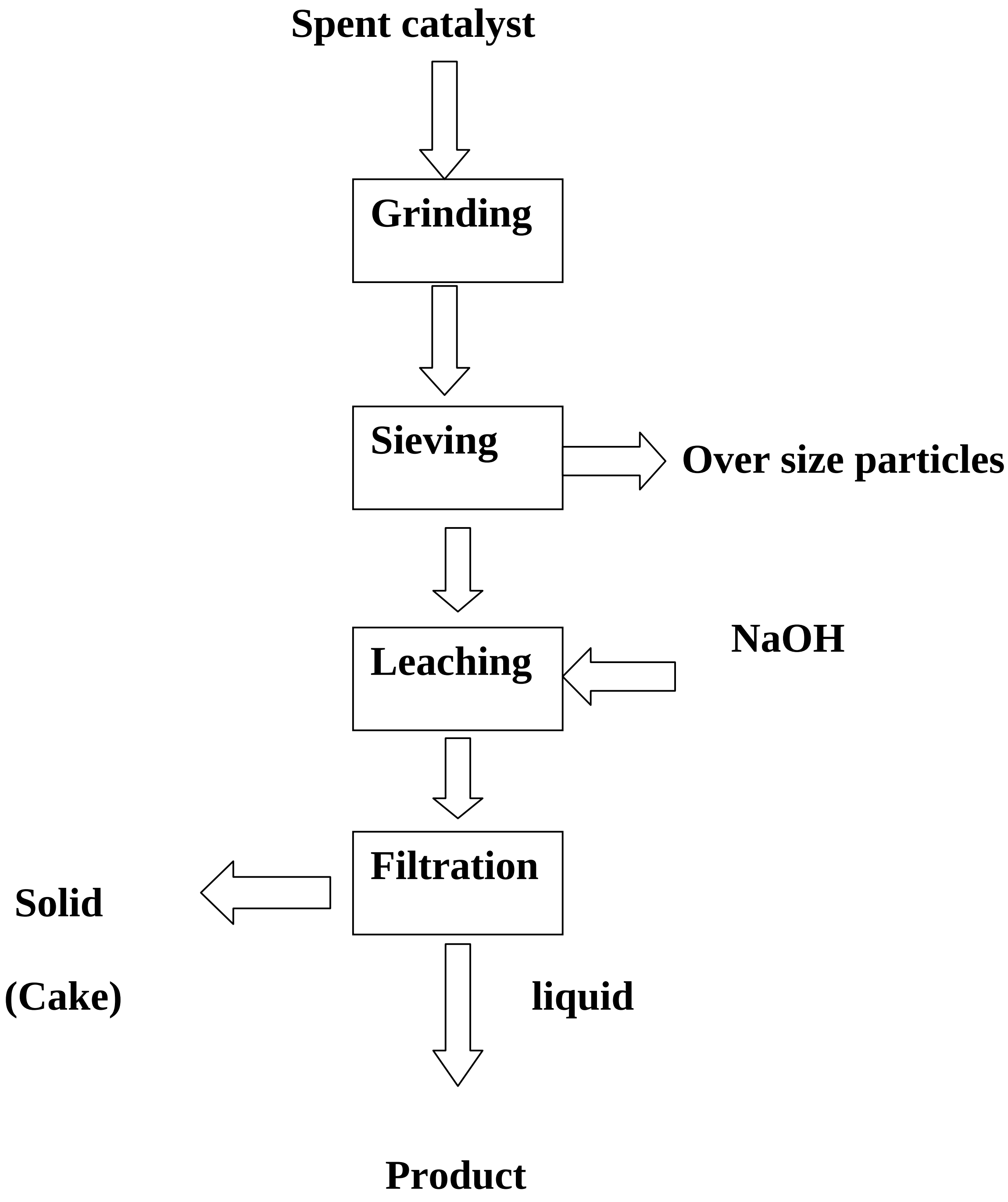

Figure (4-2): Experimental Procedure Block Diagram

5.1 Effect of Different Variables on the percentage of vanadium recovery

5.1.1 Effect of Particle Size

The particle size influences the conversion in a number of ways. The smaller the 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. If the diffusion of the solute through the porous structure of the residual solids is the controlling factor, the material should be of small size so that the distance the solute has to travel is small. On the other hand, if diffusion of the solute from the surface of the particles to the bulk of the solution is the controlling factor, a high degree of agitation of the fluid is required. In practice very fine particles should be avoided because of the expected difficulties in filtration system i.e. smaller particle size is advantageous for leaching process but it is rather unfavorable for the filtration process.

The effect of particle size on vanadium recovery at different temperature at a given time is shown in Figures 5-1 to 5-4. In these figures it can be seen that the conversion increase as the particle size decrease. Examine figure (5-3) it can be seen, maximum recovery of vanadium was obtained with particle size of 100 µm at different temperatures, 4 molar NaOH solution and 5 hours.

By comparing result with [Luis & Cury,2000] Shows that the intra-particle diffusion is strongly influenced by the particle dimension because it affects the diffusion coefficients , So that the residual vanadium content depends on material size, where tested values (35 mesh -65 mesh) , maximum recovery of vanadium was 1310 ppm at (35 mesh particle size ,25°C temperature ,200 rpm agitation speed and at 1 % sulfuric acid concentration), but at (65 mesh particle size , 25°C temperature ,200 rpm agitation speed and at 1 % sulfuric acid concentration) the vanadium conversion was 1110 ppm.

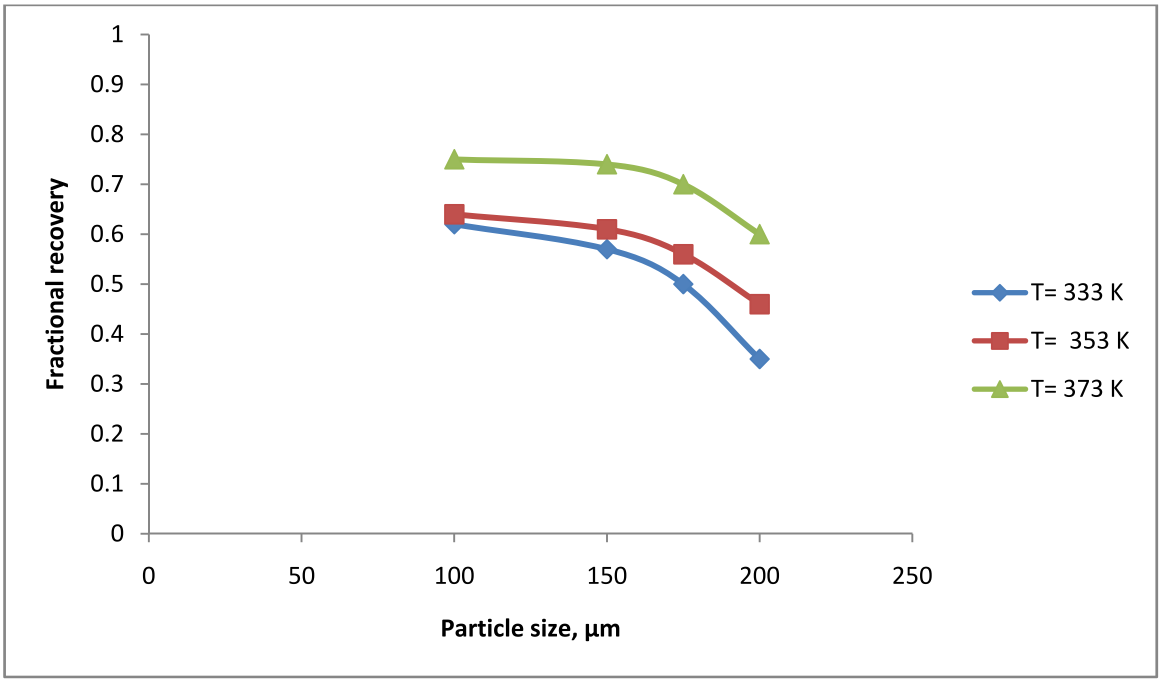

Fig. 5.1 Effect of particle size on vanadium recovery at different temperatures for 5 h and 2 molar NaOH

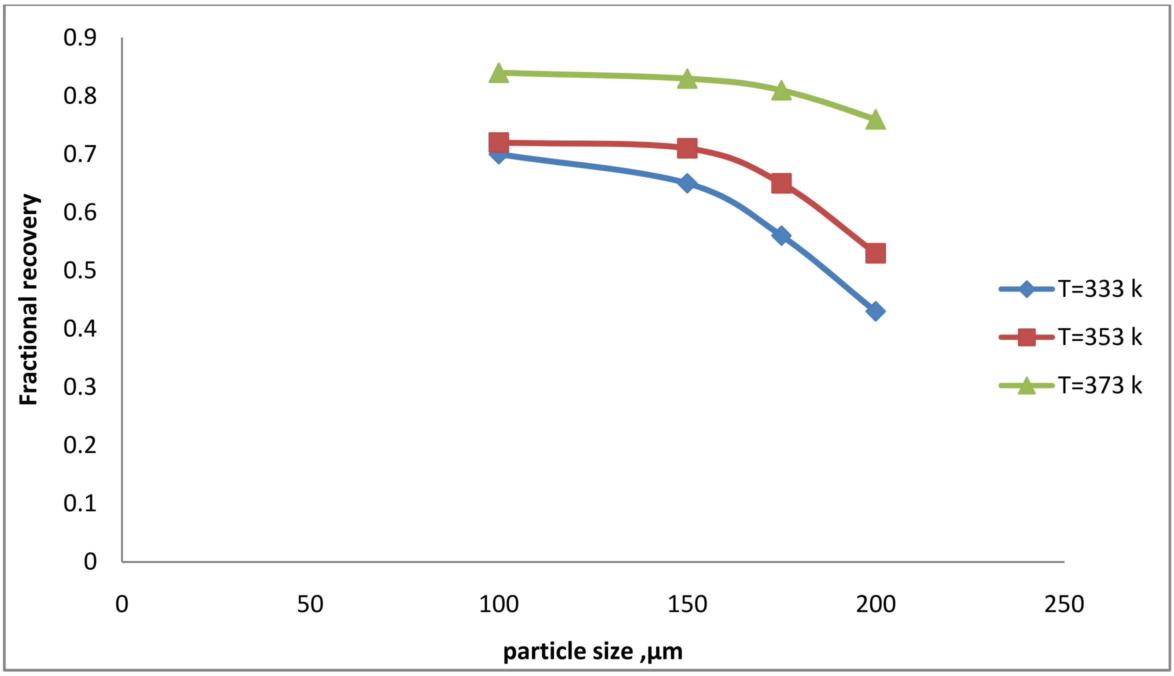

Fig. 5.2 effect of particle size on vanadium recovery at different temperatures for 5h and 3 molar NaOH

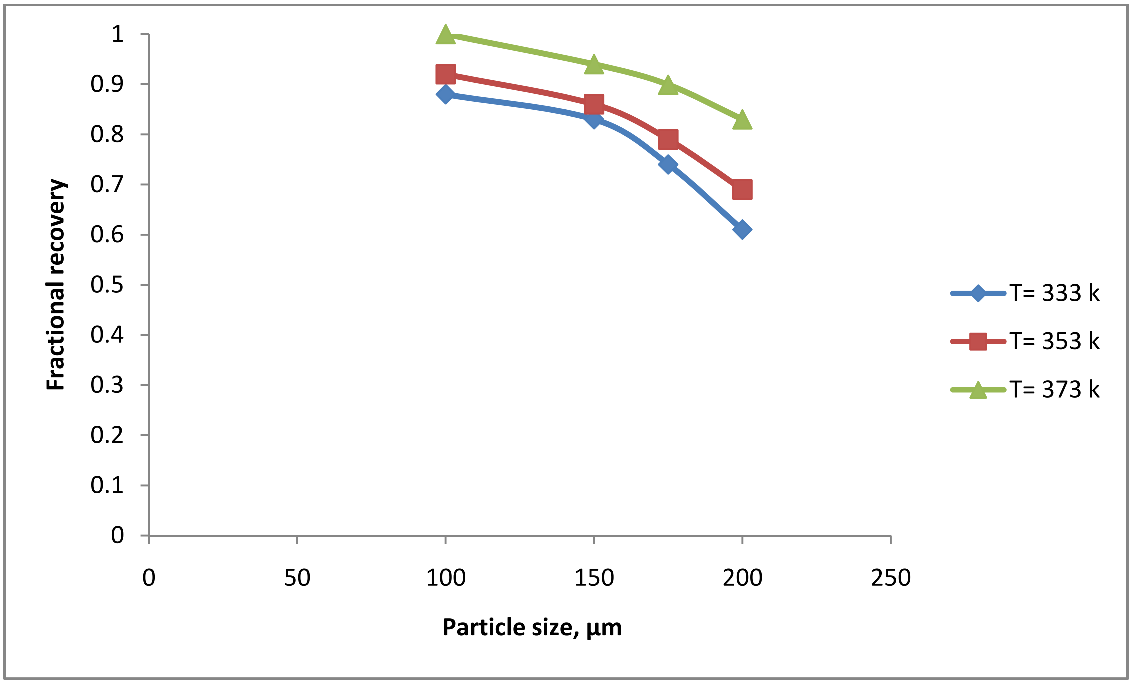

Fig. 5.3 effect of particle size on vanadium recovery at different temperatures for 5h and 4molar NaOH

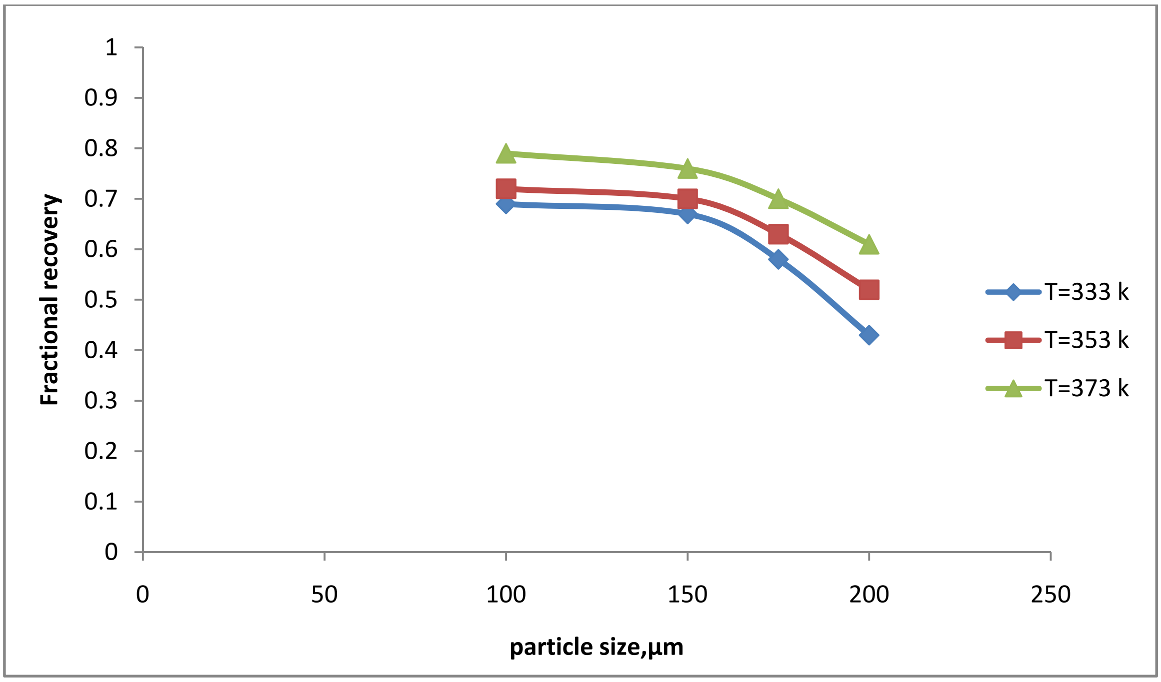

Fig. 5.4 effect of particle size on vanadium recovery at different temperatures for 1h and 4molar NaOH

5.1.2 Effect of Temperature

The temperature influences the vanadium recovery 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 coincided with the definition of the diffusivity).

Experiments at different temperatures should easily distinguish between ash or film diffusion on the one hand and chemical reaction on the other hand as the controlling step, this phenomenon is in a very good agreement with figure (5-16) at 100˚C, 100 µm, and after 5 hr it can be seen the chemical reaction is the controlling step.

The effect of temperature on vanadium recovery at different molarity at a given particle size is shown in figures (5-5 to 5-7). Examining these figures it can be shown that increasing temperature will increase the vanadium recovery.

By comparing with result in [Luis & Cury,2000] finding that the Leaching velocity of residual vanadium content showed to be influenced by temperature where Tested values from (25ºC to 55ºC) , where vanadium conversion was 1310 ppm at (35 mesh particle size ,25°C temperature ,200 rpm agitation speed and at 1 % sulfuric acid concentration), but at (35 mesh particle size , 55°C temperature ,200 rpm agitation speed and at 1 % sulfuric acid concentration) the vanadium conversion was 1190 ppm .

[S. Khorfan et al. , 2002] the effect of temperature was investigated by varying the temperature from 60 ºC to 100 ºC with other conditions constant (mixing time = 60 min, solid/liquid = 1/10 g/ml, sulphuric acid 15% v/v). It is clear that the efficiency increases negligibly after 80 ◦C, so the temperature was fixed at 100 ºC for other experiments.

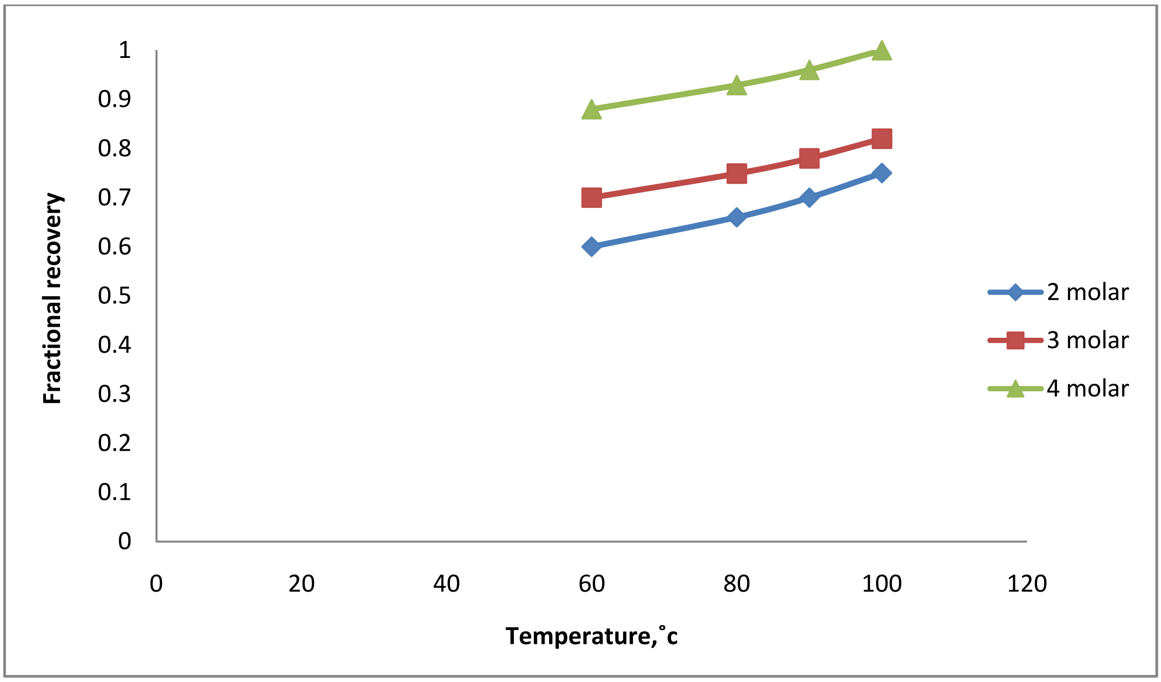

Fig. 5.5 Effect of temperature on vanadium recovery at different particle size for 5 h and 100 µm.

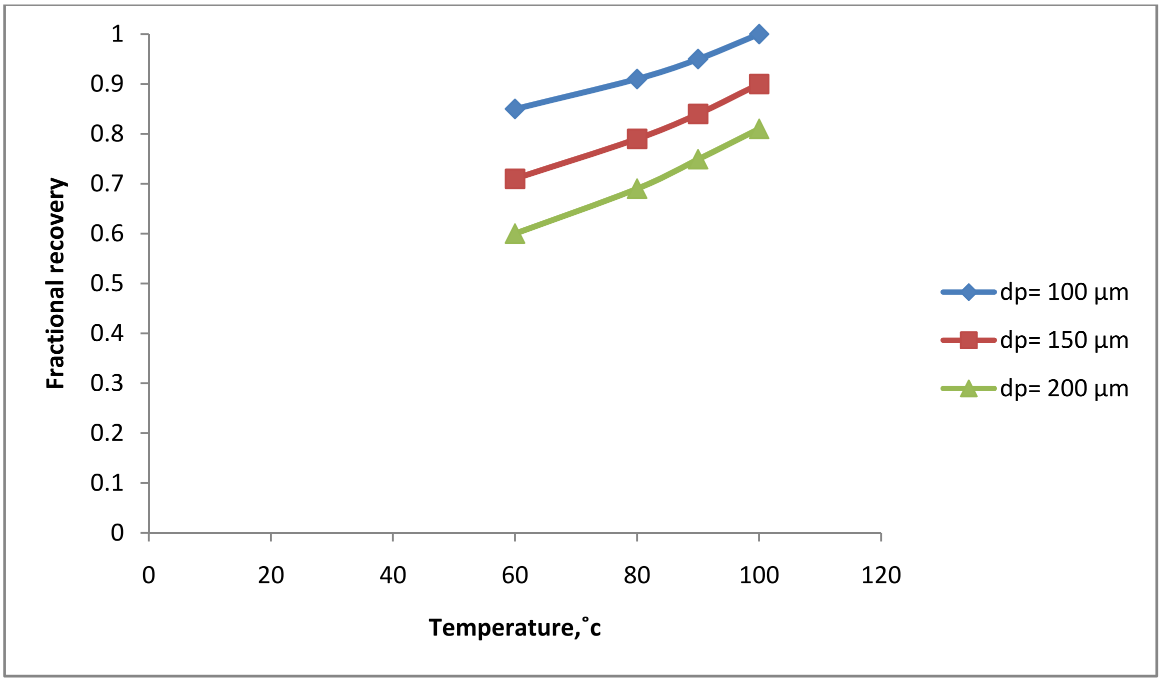

Fig. 5.6 Effect of temperature on vanadium recovery at different particle size for 4 molar and 5h

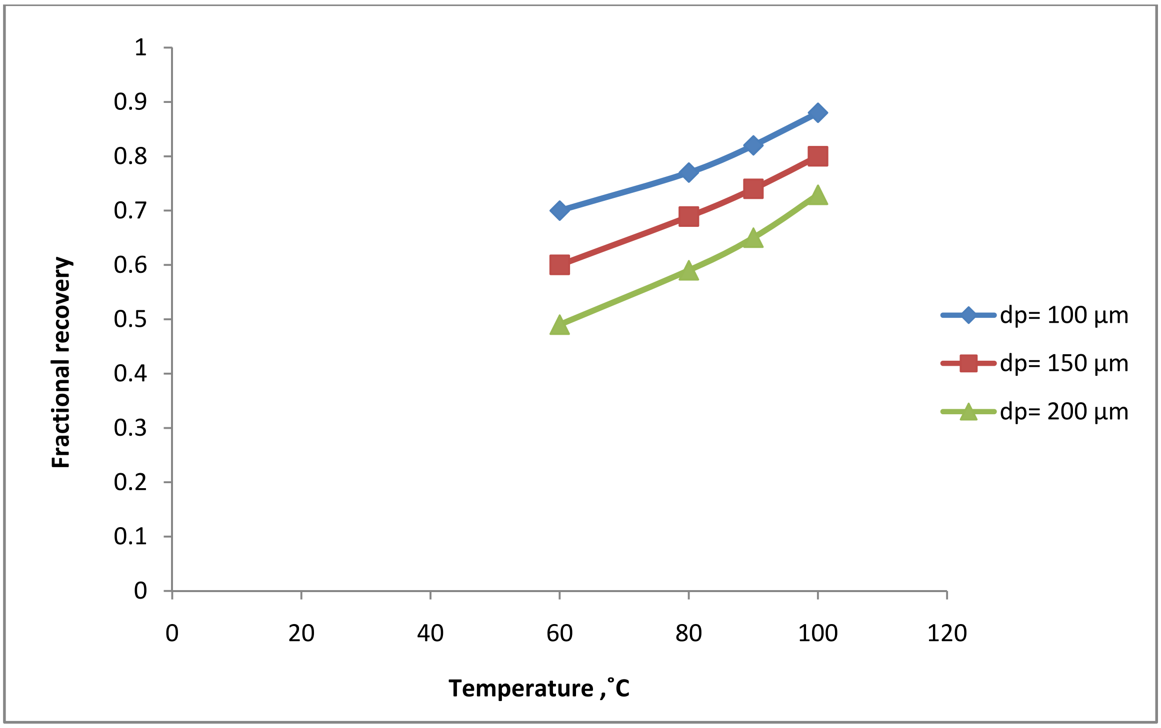

Fig. 5.7 Effect of temperature on vanadium recovery at different particle size for 3molar and 5h

5.1.3 Effect of NaOH molarity

In leaching process equations (3-10),(3-18),and (3-23) describe the external diffusion rate, diffusion through product and reaction rate respectively. From these equation the rate is greatly depend on NaOH concentration. Plotting the percentage of vanadium recovery versus NaOH molarity ,for different temperature at given particle size and time is shown in figures (5-8 to 5-11). These figures show that vanadium recovery increase as the molarity of NaOH increases. Where in figure (5-11) show that the percent recovery of vanadium increases with molarity increasing at all temperatures studied for particle size 100 μm,4 molar and 5h leaching time.

By comparing with result in [Luis & Cury,2000] Leaching velocity of residual vanadium content does not depend on the sulfuric acid concentration since it plays the role of reactant it influences the kinetic ,where tested values from (1% and 10%), where vanadium conversion was 1310 ppm at (35 mesh particle size ,25°C temperature ,200 rpm agitation speed and at 1 % sulfuric acid concentration), but at (35 mesh particle size , 25°C temperature ,200 rpm agitation speed and at 10 % sulfuric acid concentration) the vanadium conversion was 1300 ppm.

[S. Khorfan et al. ,2002] finding that Different solid/liquid (S/L) ratios were studied using sulphuric acid 15% v/v and a mixing time of one hour at 100 ◦C. three phase ratios S/L = 1/15, 1/10, 1/5 g/ml give the highest efficiency but S/L = 1/5 g/ml was found to be the best as a result of the trade-off between the vanadium recovery (96.8%) and the concentration of V_2O_5% in the sulphuric acid solution (0.71%).One liter of leaching solution (0.71%V_2O_5) was prepared by adopting the previous typical conditions (mixing time = 60 min, solid/liquid = 1/5 g/ml, sulphuric acid 15% v/v).

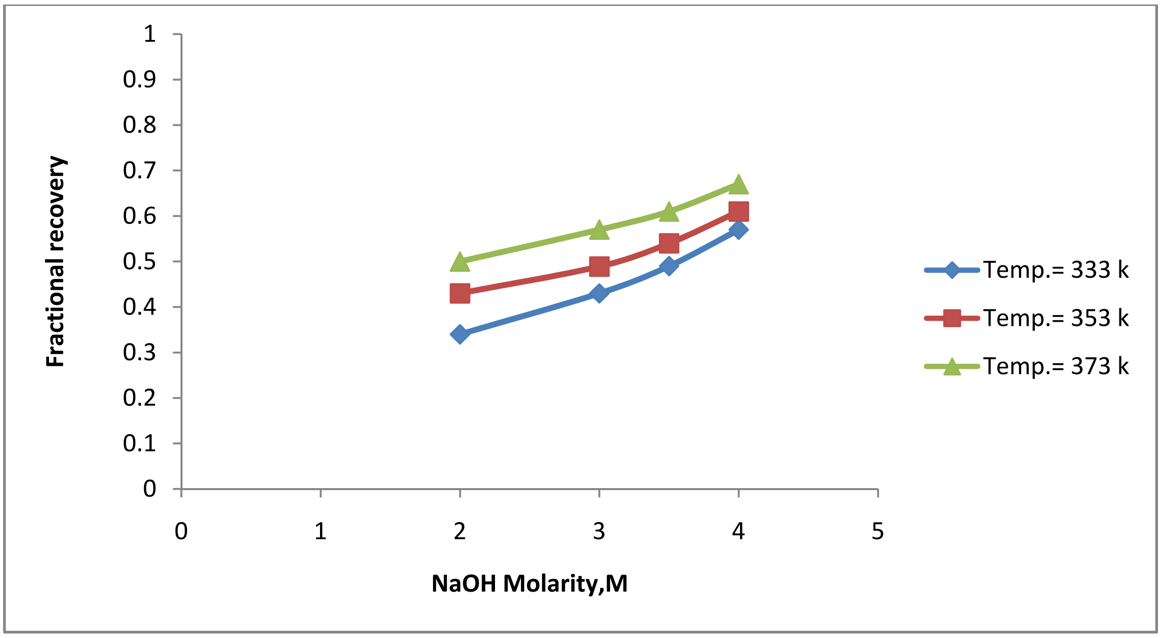

Fig.5.8 Effect of NaOH molarity on vanadium recovery at different temperature for 1 h and 150 μm

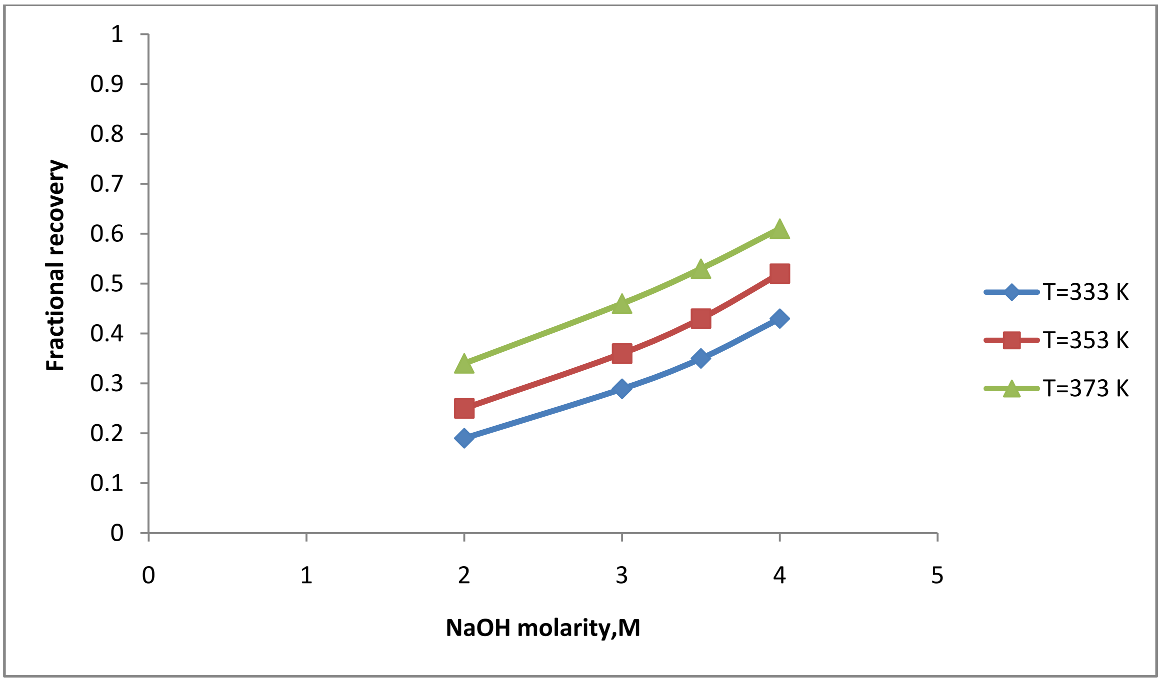

Fig.5.9 Effect of NaOH molarity on vanadium recovery at different temperature for 1h and 200 μm

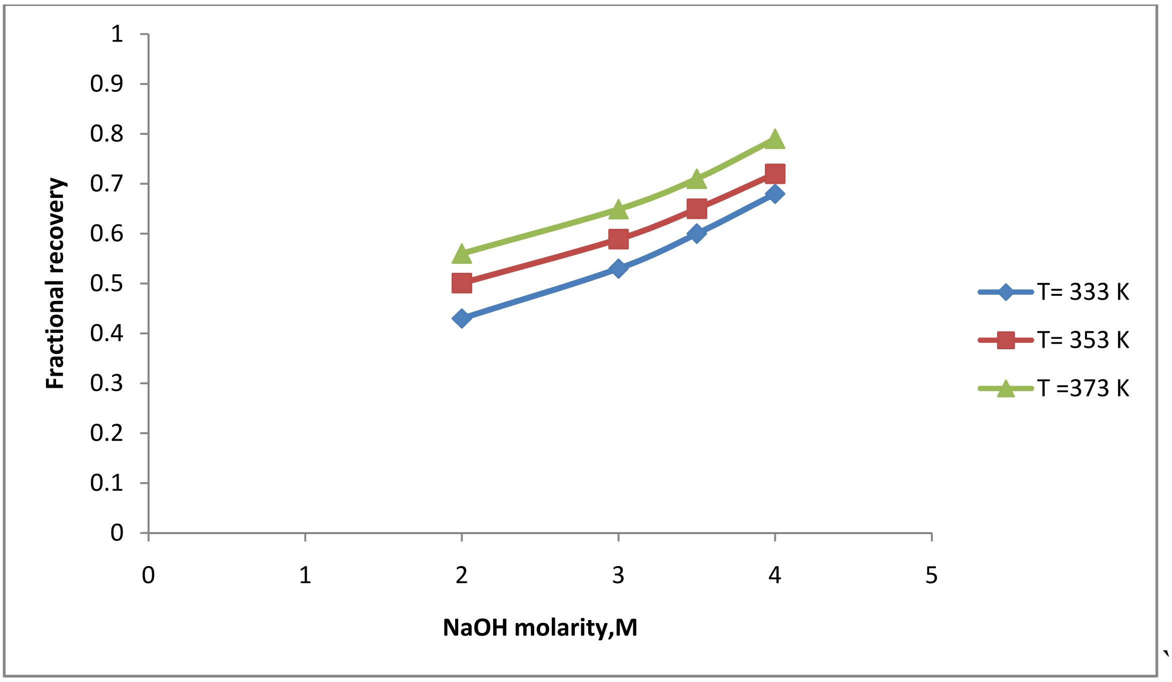

Fig.5.10 Effect of NaOH molarity on vanadium recovery at different temperature for 1 h and 100 μm

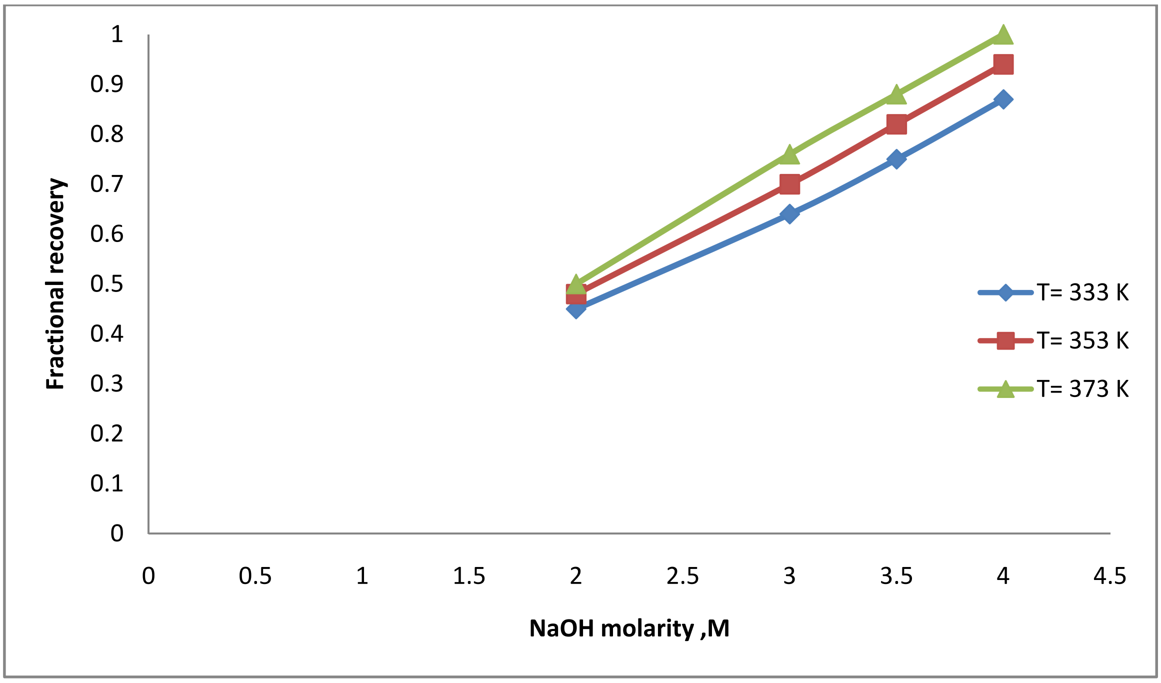

Fig.5.11 Effect of NaOH molarity on vanadium recovery at different temperature for 5 h and 100 μm

5.1.4 Leaching Time

Figures 5-12 to 5-14 show the plots of percentage of vanadium recovery versus time for different temperatures and a given particle size and NaOH molarity.

It is clear from these figures that the best leaching time which lead to maximum recovery of vanadium is greatly dependant on the specific conditions of test i.e particle size, molarity of NaOH and temperature of test. Examination of figure (5-14) shows that the maximum recovery percentage was at 100 μm particle size and 4 molar NaOH, where the best leaching time was found to be 5 hr at different temperatures.

By comparing with result in [Luis & Cury, 2000] Complementary experiments made possible to determine the equilibrium moisture of 49% in several filtration cakes which shows that the counter current leaching (with two stages with 20 minutes of residence time each) followed by washing (four stages) give the desired result. Extracted vanadium is precipitated by pH increase, so that the solution can be recycled.

[S. Khorfan et al. ,2002] showed that the leaching was carried out by varying the time of mixing from 10 min to 4 hours while keeping other conditions constant (T = 100 ◦C, solid/liquid = 1/10 g/ml,sulphuric acid 15% v/v). The efficiency was constant after 30 min so it is enough to fix the mixing time at one hour for other experiments.

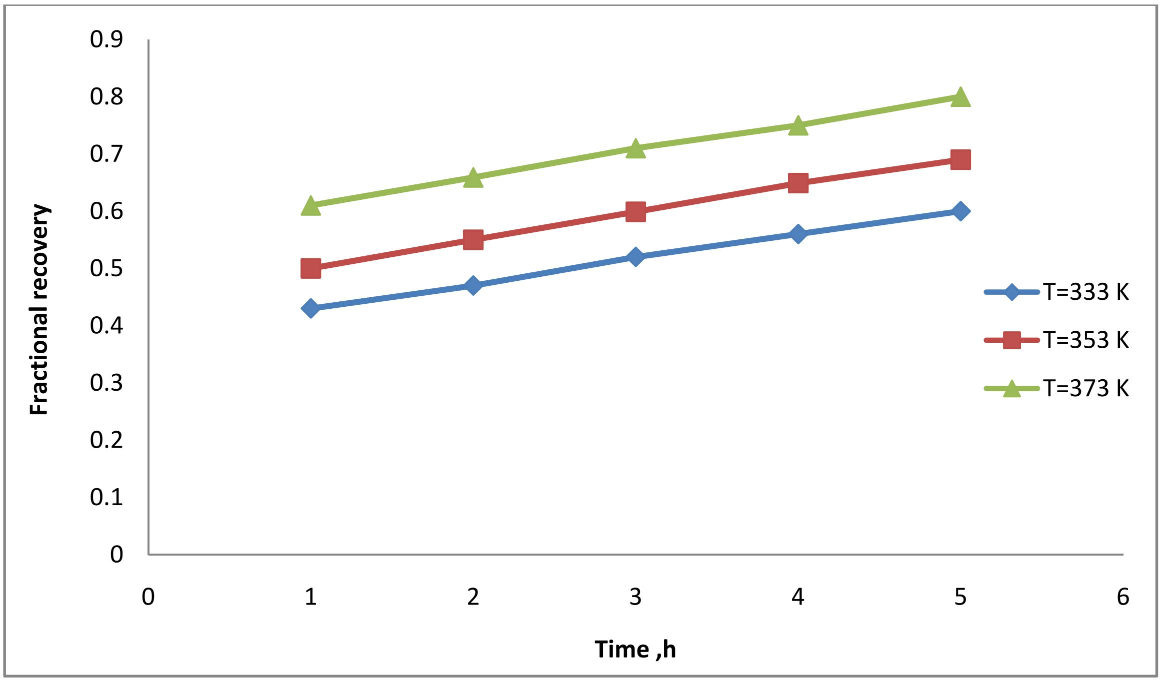

Fig. 5.12 effect of time on vanadium recovery at different temperatures for 200 µm particle size and 4 molar NaOH

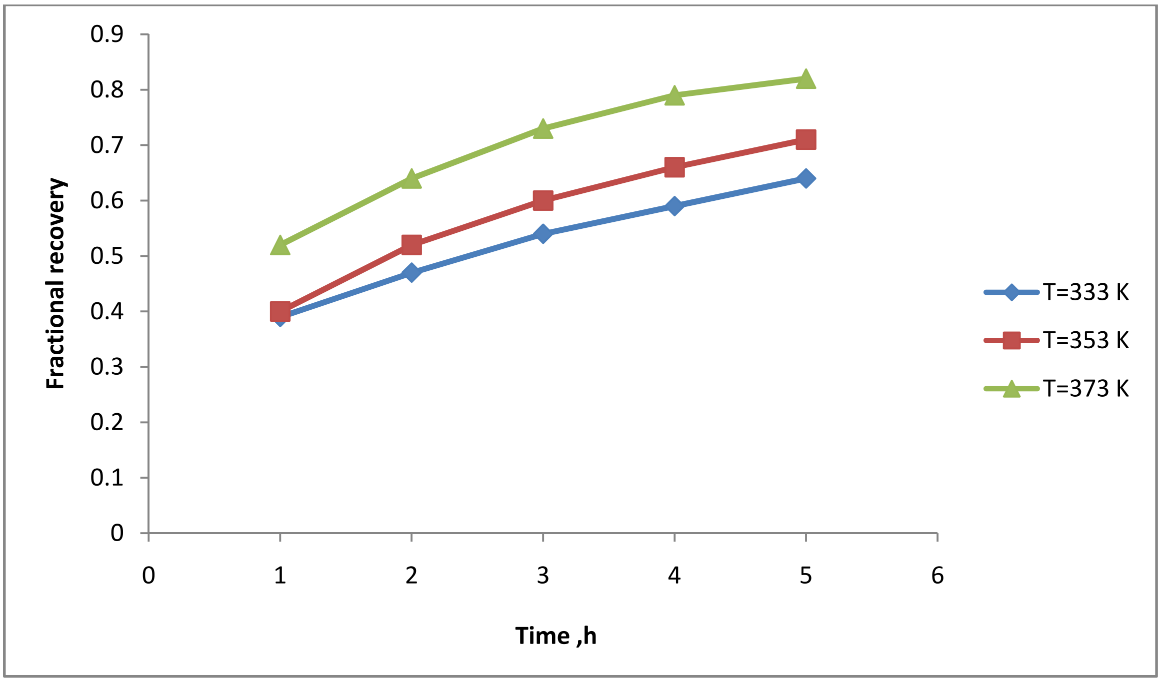

Fig. 5.13 effect of time on vanadium recovery at different temperatures for 150 µm particle size and 4 molar NaOH.

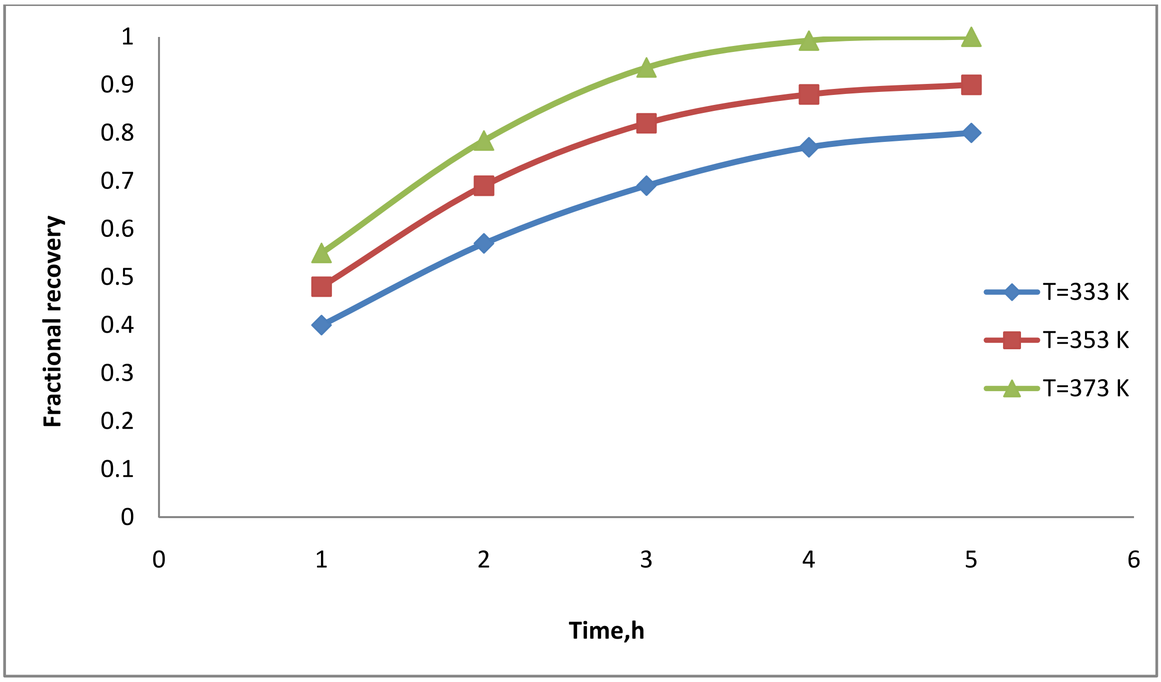

Fig. 5.14 effect of time on vanadium recovery at different temperatures for 100µm particle size and 4 molar NaOH

5.2 Mathematical Expression

A mathematical expression was found by utilizing experimental data, to relate the effect of different variables studied on the percentage recovery of Vanadium. This was achieved by relating the various variables (X_1, X_2 , X_3 and X_4) by a simple multivariable polynomial,.Where Temperature X_1 , Particle size X_2 , Time X_3, and molarity X_4. which has the general form :

$$\mathrm{Y} = Ao + \sum_{i=1}^{n} Aixi + \sum_{i=1}^{n} Bi\, Xi^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} CijXiXj \text{ .... (5-1)}$$

A second order polynomial mathematical correlation was employed in

Equation (5-1) can be represented as follow:

$$\mathrm{y} = \mathrm{A_o} + (\mathrm{A_1} * \mathrm{X_1}) + (\mathrm{A_2} * \mathrm{X_2}) + (\mathrm{A_3} * \mathrm{X_3}) + (\mathrm{A_4} * \mathrm{X_4}) + (\mathrm{A_5} * \mathrm{X_1^2}) + (\mathrm{A_6} * \mathrm{X_2^2}) + (\mathrm{A_7} * \mathrm{X_3^2}) + (\mathrm{A_8} * \mathrm{X_4^2}) + (\mathrm{A_9} * \mathrm{X_1} * \mathrm{X_2}) + (\mathrm{A_{10}} * \mathrm{X_1} * \mathrm{X_3}) + (\mathrm{A_{11}} * \mathrm{X_1} * \mathrm{X_4}) + (\mathrm{A_{12}} * \mathrm{X_2} * \mathrm{X_3}) + (\mathrm{A_{13}} * \mathrm{X_2} * \mathrm{X_4}) + (\mathrm{A_{14}} * \mathrm{X_3} * \mathrm{X_4})$$

. ..... (5-2)

The least squares method for multivariable was adopted to estimate various coefficient, the results are summarized in table (5-1)

After the coefficient values of Equation 5.2 were calculated by using least square method , it was possible to compute values of vanadium conversion (Y_i) and the corresponding residual $e_i=Y-Y_i$.

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

$$\gamma = No.of\ \exp eriments - No.of\ coefficients\ in\ Equation \qquad \ldots (5.3)$$

And

$$S_r^2 = \sum \frac{e_i^2}{\gamma} \qquad \ldots (5.4)$$

Table 5.1: least sequares coefficients

Correlation Coefficient R = 0.9893

Variance = 0.9787

Function	A_i	**Estimate**	**Variable**
1	A_0	45.04899	-
2	A_1	-0.55955	***X1***
3	A_2	-0.35131	***X2***
4	A_3	18.50088	***X3***
5	A_4	25.85468	***X4***
6	A_5	0.00173	X_1^2
7	A_6	0.00076	X_2^2
8	A_7	1.96742	X_3^2
9	A_8	-0.62292	X_4^2
10	A_9	-0.00013	X_1X_2
11	A_{10}	-0.06031	X_1X_3
12	A_{11}	-0.04050	X_1X_4
13	A_{12}	-0.00545	X_2X_3
14	A_{13}	0.00650	X_2X_4
15	A_{14}	0.25686	X_3X_4

5.3 Determination of the rate –controlling step

The kinetics and rate-controlling steps of a fluid-solid reaction are deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. Where the chemical step is usually much more temperature-sensitive than the physical steps; hence, experiments at different temperatures should easily distinguish between ash or film diffusion on the one hand and chemical reaction on the other hand 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 ash 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.

Results of kinetic runs by comparing the experimental data with predicted curves, where its indicate the rate controlling step. Unfortunately, the difference between ash diffusion and chemical reaction as controlling steps is not great and may be masked by the scatter in experimental data [Levenspiel, 1999]. Where t is time of reaction (h), X_B is conversion of vanadium and τ is time for complete conversion. It is obvious from experimental data that the time for complete conversion (τ) is 5 h of 100µm particle size, 4 molar NaOH molarity and 100ºC, where the density (ρ) is constant.

Using equation (5-2) given the value of X_B at differents time, 100µm particle size, 4 molar NaOH molarity and temperature 100ºC, where these conditions are the optimum for complete vanadium conversion at τ =5 h

Table 5.2 t/τ versus ($1 - X_B$) at 100µm particle size and 100ºC and 4 M NaOH molarity.

t/τ	$1 - X_B^{2nd\ order\ polynomail}$
0	1
0.2	0.512
0.4	0.216
0.6	0.064
0.8	0.008
1	0

The variables influencing the leaching process are (particle size, temperature, NaOH molarity and leaching time) allowed more advantageous industrial conditions to be determined and verified that the process is chemical reaction.

Results of kinetic runs by comparing the experimental data with predicted curves in figures (3.4) ,where this comparing are shown in figure (5.16) at differents time , 100µm particle size , 4 molar NaOH molarity, temperature 100ºC , and time to complete vanadium conversion τ =5 h clearly indicate that the chemical reaction is the controlling step .

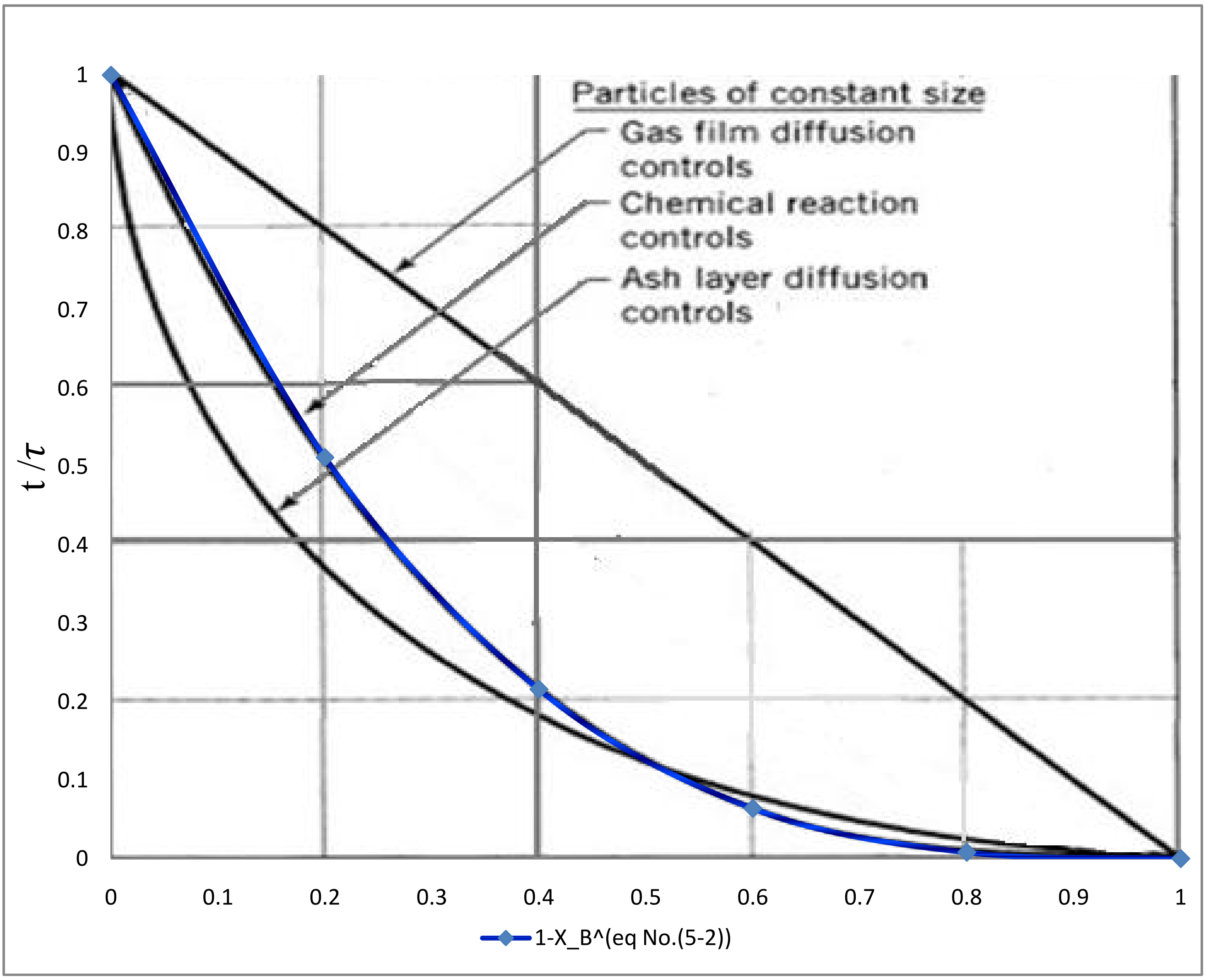

Fig. 5.15 t/τ versus ($1-X_B$) at 100μm particle size and different time,4 molar NaOH molarity, temperature 100ºC , and time for complete vanadium conversion τ =5 h

By comparing the result with [S.Khorfan et al. , 2002] Leaching velocity showed to be influenced by particle dimensions and temperature and does not depend on the sulfuric acid concentration nor agitation speed. This behavior can be explained by the fact that the slowest step of this process is the intraparticle diffusion and the reaction kinetics and also that the mass transfer from the particle to the surrounding media are minor resistances.

[Lozano and Juan ,2001] the variables influencing the leaching process are : leaching agent concentration, (Solid/Liquid) ratio, stirring speed and temperature, allowed more advantageous industrial conditions to be determined and verified that the process is diffusion controlled .

[Luis and Cury, 2000] Leaching velocity showed to be influenced by particle dimensions and temperature and does not depend on the sulfuric acid concentration nor agitation speed. This result indicates that the dominant resistance of the process is the intra-particle diffusion.

6.1 Conclusions

1. From the present investigatigation it was found that the percentage vanadium recovery was increased when :

A- Increasing temperature.
B- Increasing NaOH molarity.
C- Decreasing particle size.
D- Time increase.

2. The optimum leaching time depended greatly on specific conditions of test; temperature, particle size and NaOH molarity.
3. The selectivity of NaOH solution for the recovery of vanadium from spent catalyst was excellent.
4. At a given particle size and NaOH molarity it was found that at 100℃ the controlling step was the chemical reaction which has the highest resistance among other steps , and the (τ) for the chemical reaction equals to 5 hr. A complete vanadium recovery was achieved at (100℃, 100 µm, 5 hr and 4 molar NaOH solution).
5. A second order polynomial mathematical correlation was employed in the range of independent variables temp. (60˚C - 100˚C), particle size (100 µm - 200 µm), time up to 5 hr and molarity (2M - 4M) with correction factor of 0.9890 .

6 .2 Recommendations

1- Study the effect of solid /liquid on the vanadium recovery.
2- Study the possibility of extraction of the remaining materials from residue that will be concentrated after the recovery of vanadium.
3- Study the effect of pressure on the vanadium recovery.

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Appendix A

Raw Data

30	373	150	2	5	74.31
31	333	100	2	1	36.58
32	333	100	2	2	46.19
33	333	100	2	3	51.02
34	333	100	2	4	58.30
35	333	100	2	5	62.99
36	353	100	2	1	40.71
37	353	100	2	2	44.15
38	353	100	2	3	51.70
39	353	100	2	4	59.99
40	353	100	2	5	64.08
41	373	100	2	1	46.99
42	373	100	2	2	50.00
43	373	100	2	3	56.80
44	373	100	2	4	67.38
45	373	100	2	5	75.80
46	333	200	3	1	23.55
47	333	200	3	2	29.38
48	333	200	3	3	34.75
49	333	200	3	4	39.44
50	333	200	3	5	43.84
51	353	200	3	1	30.89
52	353	200	3	2	37.25
53	353	200	3	3	45.94
54	353	200	3	4	58.75
55	353	200	3	5	63.45
56	373	200	3	1	47.75
57	373	200	3	2	52.25
58	373	200	3	3	63.63
59	373	200	3	4	79.93
60	373	200	3	5	86.31

Appendix A. Raw Data

61	333	150	3	1	34.6
62	333	150	3	2	41.94
63	333	150	3	3	54.25
64	333	150	3	4	68.03
65	333	150	3	5	75.25
66	353	150	3	1	44.75
67	353	150	3	2	57.25
68	353	150	3	3	68.50
69	353	150	3	4	73.75
70	353	150	3	5	81.34
71	373	150	3	1	53.81
72	373	150	3	2	59.67
73	373	150	3	3	68.36
74	373	150	3	4	72.8
75	373	150	3	5	93.33
76	333	100	3	1	44.90
77	333	100	3	2	53.52
78	333	100	3	3	66.09
79	333	100	3	4	73.34
80	333	100	3	5	80.83
81	353	100	3	1	49.78
82	353	100	3	2	56.31
83	353	100	3	3	68.94
84	353	100	3	4	79.12
85	353	100	3	5	82.47
86	373	100	3	1	52.99
87	373	100	3	2	68.79
88	373	100	3	3	77.91
89	373	100	3	4	89.02
90	373	100	3	5	94.00
91	333	200	4	1	30.35

92	333	200	4	2	37.71
93	333	200	4	3	46.08
94	333	200	4	4	53.09
95	333	200	4	5	61.39
96	353	200	4	1	36.87
97	353	200	4	2	48.05
98	353	200	4	3	55.01
99	353	200	4	4	62.39
100	353	200	4	5	69.19
101	373	200	4	1	49.38
102	373	200	4	2	58.89
103	373	200	4	3	65.67
104	373	200	4	4	74.06
105	373	200	4	5	83.56
106	333	150	4	1	48.99
107	333	150	4	2	56.73
108	333	150	4	3	68.29
109	333	150	4	4	78.67
110	333	150	4	5	83.49
111	353	150	4	1	52.22
112	353	150	4	2	62.49
113	353	150	4	3	74.39
114	353	150	4	4	83.20
115	353	150	4	5	86.01
116	373	150	4	1	60.24
117	373	150	4	2	68.11
118	373	150	4	3	77.50
119	373	150	4	4	88.56
120	373	150	4	5	97.01
121	333	100	4	1	59.11
122	333	100	4	2	66.9

Appendix A Raw Data

123	333	100	4	3	79.57
124	333	100	4	4	83.83
125	333	100	4	5	88.99
126	353	100	4	1	62.55
127	353	100	4	2	68.20
128	353	100	4	3	77.36
129	353	100	4	4	84.04
130	353	100	4	5	90.66
131	373	100	4	1	67.4
132	373	100	4	2	79.9
133	373	100	4	3	86.35
134	373	100	4	4	98.71
135	373	100	4	5	100

Appendix A

Raw Data

No.	Temperature (X_1), K	Particle size (X_2), µm	Time (X_3), h	Molarity (X4), M	Experimental conversion , %
1	333	200	2	1	19.23
2	333	200	2	2	22.52
3	333	200	2	3	25.25
4	333	200	2	4	30.95
5	333	200	2	5	34.30
6	353	200	2	1	23.63
7	353	200	2	2	26.26
8	353	200	2	3	30.25
9	353	200	2	4	37.85
10	353	200	2	5	46.25
11	373	200	2	1	34.38
12	373	200	2	2	40.25
13	373	200	2	3	49.03
14	373	200	2	4	56.31
15	373	200	2	5	67.38
16	333	150	2	1	27.90
17	333	150	2	2	36.99
18	333	150	2	3	42.71
19	333	150	2	4	50.03
20	333	150	2	5	57.00
21	353	150	2	1	33.98
22	353	150	2	2	39.09
23	353	150	2	3	47.89
24	353	150	2	4	55.90
25	353	150	2	5	61.20
26	373	150	2	1	39.12
27	373	150	2	2	45.79
28	373	150	2	3	56.45
29	373	150	2	4	68.30

شكر و تقدير

بعد الشكر والحمد لله عز وجل أود أن أتقدم بالشكر الجزيل للدكتور خالد مخلف موسى لما بذلهُ من جهد وتعب من اجل إخراج هذا البحث بصورتهُ المتكامله ولما قدمهُ من توجيهات وإرشادات سديدة طيلة مدة البحث .

كما وأتقدم بالشكر الجزيل إلى زوجي المهندس اوس احمد وعائلتي (أبي وأمي بالأخص) وزملائي وكل من ساهم في انجاز هذا البحث .

تجريبية وحركية للاسترداد الفناديوم من مخلفات المحفز المستهلك استعمال الصودا الحارقة

رسالة

مقدمة إلى كلية الهندسة في جامعة النهرين وهي جزء من متطلبات نيل درجة
ماجستيرعلوم في الهندسة الكيمياوية

إعداد

صفا كاظم حسين

(بكالوريوس علوم في الهندسة الكيمياويه ٢٠٠٦)

ذو الحجة ١٤٣٠

تشرين الثاني ٢٠٠٩