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Ranine El Hage, Fabien Chauvet, Béatrice Biscans, Laurent Cassayre, L. Maurice, et al.. Kinetic study of the dissolution of vanadyl sulfate and vanadium pentoxide in sulfuric acid aqueous solution. Chemical Engineering Science, 2019, 199, pp.123-136. 10.1016/j.ces.2019.01.024 . hal-02290658

**HAL Id: hal-02290658**

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### **To cite this version:**

El Hage, Ranine<sup>ORCID</sup> and Chauvet, Fabien<sup>ORCID</sup> and Biscans, Béatrice<sup>ORCID</sup> and Cassayre, Laurent<sup>ORCID</sup> and Maurice, L. and Tzedakis, Théo<sup>ORCID</sup> *Kinetic study of the dissolution of vanadyl sulfate and vanadium pentoxide in sulfuric acid aqueous solution.* (2019) *Chemical Engineering Science*, 199. 123-136. ISSN 0009-2509

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# Kinetic study of the dissolution of vanadyl sulfate and vanadium pentoxide in sulfuric acid aqueous solution

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## HIGHLIGHTS

- Vanadium (IV) sulfate  $\text{VO}_2\text{SO}_4$  and vanadium (V) pentoxide  $\text{V}_2\text{O}_5$  dissolution.
- Temporal evolution of the concentrations of  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  at various temperatures.
- Understanding the dissolution limitations:  $\text{V}^{\text{IV}} \rightarrow$  mass transfer;  $\text{V}^{\text{V}} \rightarrow$  reaction with  $\text{H}^+$ .
- Simple kinetic models to predict the evolution of  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  concentrations.

## ARTICLE INFO

### Keywords:

Vanadyl sulfate  
Vanadium pentoxide  
Dissolution kinetics  
Vanadium redox battery  
Solubility

## ABSTRACT

The study deals with the 'vanadium (IV) sulfate' and 'vanadium (V) pentoxide' dissolution processes in 3 M  $\text{H}_2\text{SO}_4$  aqueous media. Several measurements of the concentration of dissolved  $\text{VO}^{2+}$  and  $\text{VO}_2^+$  were achieved in the range of 0–40 °C, and allowed to understand the limitations of the dissolution process ('endothermic' mass transport for  $\text{VO}_2\text{SO}_4$  and 'exothermic' reaction with the proton for  $\text{V}_2\text{O}_5$ ). In addition, simple models were proposed (diffusion/accumulation for  $\text{VO}_2\text{SO}_4$  and kinetic rate for  $\text{V}_2\text{O}_5$ ) and their resolution leads to theoretical kinetic equations describing the temporal evolution of these concentrations with satisfactory agreement with the experimental curves. Solubility's data and their temperature dependence were determined for both vanadium compounds involved.

## 1. Introduction

Renewable energy storage studies have expanded in the past decades due to the rapid increase in energy consumption, limited fossil fuels reserves and growing ecological concerns of their impact on health and environment.

Only a very limited number of systems enable energy storage such as thermal storage, pumped hydropower and compressed air energy storage (Amirante et al., 2017; Ding et al., 2009). Electrochemical storage constitutes an interesting alternative and recently the Redox Flow Battery (RFB) acquired a great importance as they have the particularity of converting and storing energy by using electroactive species dissolved in electrolyte solutions (Wang et al., 2013; Leung et al., 2012). The most spread RFB is the "all

vanadium" redox flow battery (VRFB) developed in the 1980's by Rychcik and Skyllas Kazacos (1988), Skyllas Kazacos et al. (1988) and has been widely explored since (Cunha et al., 2015; Skyllas Kazacos et al., 2016, 2015, 2013).

The battery was introduced to overcome the problem of cross contamination of electrolytes, inducing capacity losses reported primarily by NASA researches in the 1970s for the Fe-Cr system (Thaller, 1977, 1974). Given that the same element in different oxidation states is used in both compartments of the VRFB, no contamination of the active material will occur in case ions cross the ionic separator. The redox couples employed are  $\text{V}^{\text{III}}/\text{V}^{\text{II}}$  and  $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$  for the negative and the positive half cells respectively (Sum et al., 1985; Sum and Skyllas Kazacos, 1985), and the only redox reactions involved are thus the valence changes of the vanadium ions. The electrolyte solutions are usually prepared in 2–3 M sulfuric acid, even if other electrolytes have been investigated (generation 2 and 3 of the VRB) (Skyllas Kazacos et al., 2007). The VRB is characterized by a long life span (>10,000 cycles) (Ashby and Polyblank, 2012), low maintenance cost and deep discharge

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## Nomenclature

$A_{(765\text{ nm})}$	absorbance at the wave length of 765 nm	PES	polyether sulfone
$A$	Arrhenius pre exponential factor	$R^0$	initial radius of the particle (m)
$a_{\text{VOSO}_4 \text{ solid}}$	activity of the solid compound	$R_{(t)}$	radius of the particle at the dissolution time $t$ (m)
$a$	constant (Leveque correlation)	$r^0$	initial reaction rate (mol L <sup>-1</sup> s <sup>-1</sup> )
$A_1, A_2, A_3$ and $A_4$	constants (defined in Appendix A)	$r_{\text{global}}$	total rate of the reaction of the dissolution of V <sub>2</sub> O <sub>5</sub> (mol L <sup>-1</sup> s <sup>-1</sup> )
$C_{\text{bulk}}$	concentration of VO <sup>2+</sup> in the bulk (M)	RFB	Redox Flow Battery
$C_{\text{surface}}$	$C_{\text{saturation}}$ superficial concentration of VO <sup>2+</sup> , assumed at saturation (M)	$Re$	Reynolds number $\frac{d_p \times u}{\nu}$ $d_p \times \bar{u} \times \frac{\rho}{\mu}$
$d_p$	particle diameter at time $t$ (μm)	SEM	scanning electron microscope
$D$	diffusion coefficient (m <sup>2</sup> /s)	$S$	surface of particles involved in the dissolution process (m <sup>2</sup> )
$E_a$	activation energy (J/mol)	$Sc$	Schmidt number = $\nu/D$
$e_{(t)}$	thickness of the spherical crown film, function of the time (m)	$Sh$	Sherwood number $(Sh = \frac{k_{(t)} \times d_p}{D})$
$\epsilon$	absorptivity (cm <sup>-1</sup> M <sup>-1</sup> )	$t$	dissolution time (expressed in 's' for VOSO <sub>4</sub> and in 'h' for V <sub>2</sub> O <sub>5</sub> )
$\Delta_R H$	reaction enthalpy (J/mol)	$\bar{u}$	average rate of the liquid around the solid particle calculated from the stirring rate (m/s), assumed constant during the experiment time
$j$	number of iterations taken as 100	$\nu$	kinematic viscosity (m <sup>2</sup> /s) $\mu/\rho$
$k$	kinetic constant following the Arrhenius law (unit function of the reaction order)	$\Delta U$	internal energy (J/mol)
$k_{(t)}$	$\frac{D}{e_{(t)}}$ mass transfer coefficient of the VO <sup>2+</sup> around the solid particle of VOSO <sub>4</sub> (m <sup>-1</sup> s)	VRFB	Vanadium Redox Flow Battery
$m$	moles number of dissolved VOSO <sub>4</sub> (to VO <sup>2+</sup> ) into the bulk	$V$	solid volume present in the solution at time $t$ (m <sup>3</sup> )
$M$	molar mass of the solid VOSO <sub>4</sub> 5H <sub>2</sub> O (kg/mol)	$V_l$	total volume of the solution (including both the liquid and the powder)
$N$	number of VOSO <sub>4</sub> particles having a certain initial radius $R^0$	$\omega$	stirring rate (rpm)
$n^{\circ(V)}$	initial moles number of V <sub>2</sub> O <sub>5</sub> (mol)	$X$	moles number of V <sub>2</sub> O <sub>5</sub> dissolved at time $t$
$n^{\circ(H)}$	initial moles number of H <sup>+</sup> (mol)		
$\rho$	specific gravity of the powder (kg/m <sup>3</sup> )		
PTFE	polytetrafluoroethylene		

capability (Vijayakumar et al., 2013). The energy density of the battery is largely depending on the volume and concentration of the vanadium electrolytic solutions and numerous authors studied the effect of the composition of electrolyte solutions (Choi et al., 2017; Skyllas Kazacos et al., 2016) on the performance of the battery.

Despite that, stable solutions with vanadium concentrations higher than 2 M could not be achieved in the working conditions of the VRB, limiting the quantity of stored energy to around 40 kWh/m<sup>3</sup>.

The electrolyte in the negative electrode compartment does not seem to exhibit major limitations related to the solubility of V<sup>(III)</sup> and V<sup>(II)</sup>, but one point to mention is that V<sup>(II)</sup> is easily oxidized by air (choi et al., 2013). One important limitation encountered by the vanadium battery appears to be related to the precipitation of compounds in the positive electrode: precipitation of the V<sup>(IV)</sup> at low temperature and precipitation of the V<sup>(V)</sup> compounds at high temperature.

This fact limits the working temperature range of the VRB between 10 and 40 °C (Li et al., 2011). Precipitation of various vanadium salts and oxides was studied by several research groups and it was found that higher sulfuric acid concentrations stabilizes the V<sup>(V)</sup> solutions (Rahman, 1998) but decreases the solubility of V<sup>(II)</sup>, V<sup>(III)</sup> and V<sup>(IV)</sup>. This is attributed to the common sulfate ion effect (Skyllas Kazacos et al., 2016): increasing the total sulfate concentration shifts the equilibria (1)–(4) towards the left, leading to a lesser dissociation of the vanadium sulfate salts (Rahman and Skyllas Kazacos, 1998; Cheng, 1991) and to the precipitation of the salts in solution.



As mentioned by Rahman and Skyllas Kazacos (2009), vanadium (V) can precipitate after 1000 h at 50 °C and the redissolution of the oxide V<sub>2</sub>O<sub>5</sub> (Rahman, 1998) appears to be difficult. Numerous authors (Ivakin and Voronova, 1973; Vijayakumar et al., 2011; Kausar, 2002) conducted studies to understand the poor thermal stability of V<sup>(V)</sup> at high temperatures. They showed that the precipitation process of V<sub>2</sub>O<sub>5</sub> is endothermic and thus enhanced when temperature increases.

Moreover, the aqueous chemistry of vanadium (V), studied by several authors (Crans et al., 2004; Elvingson et al., 1998), inferred the presence of many species as a function of the solution's pH. It was suggested that pervanadyl or dioxovanadium cation (VO<sub>2</sub><sup>+</sup>) is the main species formed in the lower pH range (0.5–1.3) (Baes and Mesmer, 1976). However, the presence of VO<sub>3</sub> species was also reported in the concentration range of 1 M of V<sup>(V)</sup> in 5 M total sulfate (Kausar, 2002). Based on Raman spectroscopy analysis, the authors propose that VO<sub>3</sub> species are surrounded by a densely packed ionic environment of other V<sup>(V)</sup> and sulfate ions and these ions could be involved in weak or unstable complex formation with other ions. In the case of H<sup>+</sup> ions depletion, VO<sub>3</sub> tends to precipitate as a disordered V<sub>2</sub>O<sub>5</sub> aggregate (Kausar, 2002). Increasing the acid concentration enables to prevent this precipitation and favor the stabilization of V<sup>(V)</sup> in the form of VO<sub>2</sub><sup>+</sup>. However, this induces a negative effect on the overall performance of the battery because of the increasing viscosity and an enhancement of the ohmic drops resulting in the lowering of the energy efficiency (Choi et al., 2017).

Numerous works exist on the field of the vanadium battery, and one important objective is to avoid the vanadium pentoxide

precipitation. Indeed according to [Rahman \(1998\)](#) and [Rahman and Skyllas Kazacos \(2009\)](#) vanadium (V) oxide dissolution is difficult, in addition to being an endothermic dissolution ([Ivakin and Voronova, 1973](#); [Vijayakumar et al., 2011](#); [Kausar, 2002](#)). Neither the understanding of the dissolution phenomena of the vanadium compounds, nor elucidation of the corresponding mechanisms was significantly explored; the published studies do not exhibit the determination of the physical limitations in order to act upstream. Hence, the present work deals with the study of the dissolution mechanisms of two common vanadium compounds in 3 M sulfuric acid, at various temperatures (0–40 °C), stirring rates and initial particles size. Apart from being the most common concentration used for an operating battery with 2 M VOSO<sub>4</sub>, the sulfuric acid concentration (3 M) is chosen here, as a compromise between its positive effect on the dissolution of the vanadium pentoxide and its negative effect on the dissolution of vanadium sulfate ([Rahman, 1998](#)). Note also that, by increasing the sulfuric acid concentration, the solubility of the oxide increases, but this increases the viscosity of the solution leading to a pressure drop. Moreover, during the cycling of the battery and more specifically during recharge (oxidation of V<sup>(IV)</sup> to V<sup>(V)</sup>), H<sup>+</sup> ions are generated in the positive compartment leading to an increase in acidity, therefore, it is not necessary to study higher H<sub>2</sub>SO<sub>4</sub> concentrations.

To sum up, the general purpose of this study is to understand the phenomena governing the dissolution of vanadyl sulfate VOSO<sub>4</sub> and vanadium pentoxide V<sub>2</sub>O<sub>5</sub> and to establish the corresponding kinetic laws, in order to have a better control on the accidental precipitation during VRB operations.

## 2. Material and methods

### 2.1. Dissolution protocol

The chemicals used are vanadium (IV) sulfate oxide hydrate VOSO<sub>4</sub>·xH<sub>2</sub>O (99.9%), vanadium (V) pentoxide V<sub>2</sub>O<sub>5</sub> (99.6%) from Alfa Aesar, NormaPur H<sub>2</sub>SO<sub>4</sub> from Sigma Aldrich, and deionized water.

Dissolution experiments were achieved in a thermo regulated reactor (cylinder of an internal diameter = 2 cm) at constant temperature. An adequate volume of aqueous solution 3 M sulfuric acid is poured in the reactor and stirred with a 1.5 cm magnetic bar until reaching the selected temperature. Then, an excess of vanadium compound is added ( $m_{(\text{vanadyl sulfate})} = 4.559 \text{ g}$  and  $m_{(\text{vanadium pentoxide})} = 1.461 \text{ g}$ ), marking the initial time of the experiment. Stirring rate is kept constant during the experiment. At regular time intervals, aliquots are withdrawn from the solution with plastic syringes and are directly filtered twice with filters resisting to the acid media. The first filtration is performed using a polyether sulfone (PES) filter with a pore diameter of 0.23 μm, and the second one a polytetrafluoroethylene (PTFE) membrane filter (Millipore ready to use filters in plastic assembly) with a pore diameter of 0.1 μm.

The recovered filtrate is diluted and analyzed with the appropriate method.

The vanadium compounds dissolution occurs according to reactions (3) and (5) for VOSO<sub>4</sub> and V<sub>2</sub>O<sub>5</sub> respectively.



These reactions were taken into account because the species involved at the chosen concentration of H<sub>2</sub>SO<sub>4</sub> (3 M) are in agreement with the E-pH diagram indicated by [Post and Robins \(1976\)](#), and with the V<sup>(V)</sup> species distribution calculated from constants given by [Baes and Mesmer \(1976\)](#), [Guzman et al. \(2002\)](#).

### 2.2. Characterization methods

#### 2.2.1. UV visible spectrophotometry for vanadium (IV) analysis

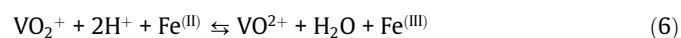
The UV VIS spectrophotometer device is a Hewlett Packard Model 8453.

According to their oxidation state, the vanadium compounds exhibit various absorption bands at the UV visible wavelengths range. However, no absorption band could be determined for the VO<sub>2</sub><sup>+</sup> species; this is why potentiometric titration was used (see next section).

For the V<sup>(IV)</sup> quantification, the absorbance was measured at a wavelength of 765 nm ([Choi et al., 2017](#)) exclusively due to VO<sup>2+</sup>. A preliminary calibration enables to obtain the A<sub>(765nm)</sub> = f([VO<sup>2+</sup>]) correlation and leads to an absorptivity ε value of 21.4 cm<sup>-1</sup> M<sup>-1</sup>, with deviations  $\frac{\Delta \epsilon}{\epsilon}$  of 0.6 and 0.25 from the values proposed by [Choi et al., 2013](#) and [Brooker et al. \(2015\)](#) respectively.

#### 2.2.2. Potentiometric titration of vanadium (V)

A potentiometric titration method is used to determine the concentration of the VO<sub>2</sub><sup>+</sup> released from the dissolved V<sub>2</sub>O<sub>5</sub> powder. The titration agent is Mohr salt, supplied by Sigma Aldrich and prepared in sulfuric acid media ([Le Flem, 1964](#)). The redox systems involved in this titration are thus VO<sub>2</sub><sup>+</sup>/VO<sup>2+</sup> and Fe<sup>(III)</sup>/Fe<sup>(II)</sup> and the titration reaction is:



The titrations are carried out using a combined Pt-Ag/AgCl/Cl electrode.

#### 2.2.3. ICP analysis

ICP analysis (Inductively Coupled Plasma; ULTIMA 2 ICP-OES) was used for total vanadium aqueous concentration determination, in order to characterize the amount of water in the commercial vanadyl sulfate powder VOSO<sub>4</sub>·xH<sub>2</sub>O.

#### 2.2.4. Morphology and particle size distribution of the powders

The scanning electron microscope (SEM) used to observe the grains morphology is a PhenomWorld XL SEM. The solid powders (V<sub>2</sub>O<sub>5</sub> and VOSO<sub>4</sub>·xH<sub>2</sub>O) were coated with a thin gold layer (using an Emiteck K550X device) prior SEM observation.

A laser diffraction particle sizing technique, using a Malvern Mastersizer 3000, was used to get the size distribution of the grains. The Malvern Mastersizer is usually used for materials ranging from hundreds of nanometers to several millimeters in size ([Fu and Sun, 2001](#)). The particle size is reported as a volume equivalent sphere diameter.

## 3. Results and discussion

### 3.1. Dissolution of vanadium (IV) sulfate

#### 3.1.1. Characterization of the initial powder

The commercial vanadyl sulfate powder VOSO<sub>4</sub>·xH<sub>2</sub>O used for the dissolution experiments is partially hydrated. Its water content x was determined by ICP at different concentrations, according to the method of determination of the vanadium concentration in an aqueous solution. The results of three analyses are found to be in the range from 5.4 to 5.6; thus taking into account the uncertainties of the analyses, the retained value of x is 5. Note that this result is in agreement with an octahedral geometry, and also with the fact claimed by [Selbin \(1965\)](#), the hydrated vanadyl sulfate exists as [VO(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, 'the vanadyl ion' in acidic solutions. In the following, VOSO<sub>4</sub>·xH<sub>2</sub>O is thus indicated as VOSO<sub>4</sub>·5H<sub>2</sub>O [Fig. 1](#).

[Fig. 1](#) presents SEM micrographs of the commercial powder. These images display aggregated and multi-shaped particles of

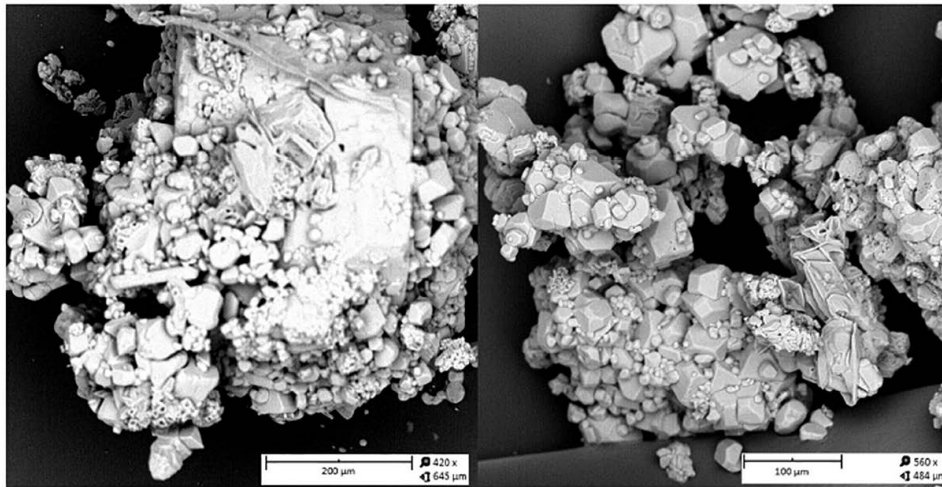


Fig. 1. SEM images of the vanadyl sulfate  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  commercial powder; 15 kV-Point; BSD full.

all sizes. Their dispersion during the dissolution in a stirred solution is expected to be easy, because of the dislocation occurring after the dissolution of the smallest particles.

The  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  particle size distribution is presented in Fig. 2. The first graph (Fig. 2 1) provides the particle size distribution of the commercial powder and clearly shows two distinct ranges: from 5 to 350  $\mu\text{m}$  and from 350  $\mu\text{m}$  to 4 mm. The commercial powder was sieved at 315  $\mu\text{m}$  and separated into two fractions, for which particle sizes are presented in Fig. 2 2 and 3. They confirm two distinct populations of particle diameter:  $d_p < 315 \mu\text{m}$  and  $d_p > 315 \mu\text{m}$ .

### 3.1.2. Temperature dependence of the dissolution kinetics

Fig. 3 gathers experimental measurements of  $\text{VO}^{2+}$  concentration in the electrolyte during the dissolution, for temperatures in the range from 5 to 30  $^\circ\text{C}$ . For all the examined temperatures, a similar temporal evolution of the concentration of  $\text{VO}^{2+}$  was observed: the concentration increases rapidly at short reaction times ( $t < 3 \text{ min}$ ) and then the dissolution slows down until equilibrium is reached, after around 10 min. When the temperature increases from 5 to 30  $^\circ\text{C}$  the initial dissolution rate increases as well.

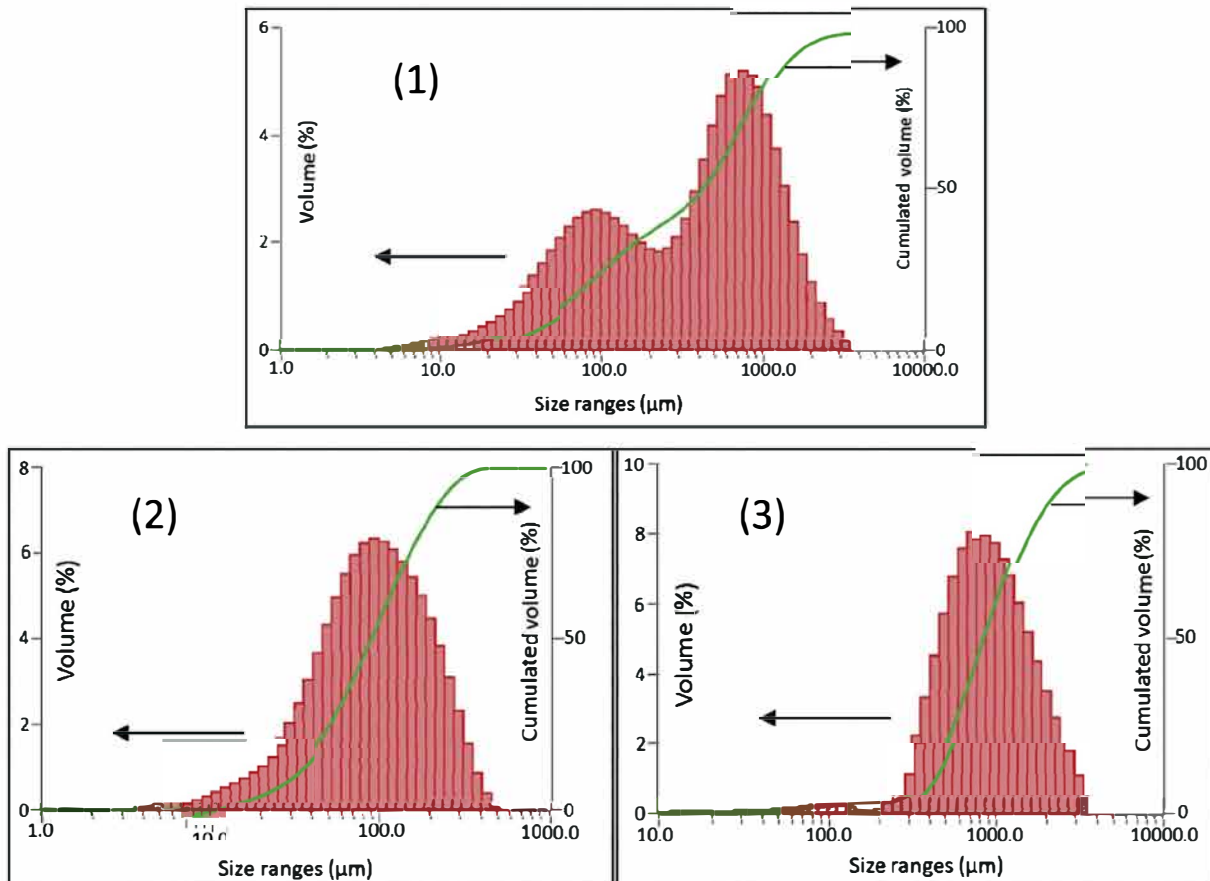


Fig. 2. Laser diffraction analysis ( $P = 3 \text{ bar}$ ; dry mode) showing the  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  size distribution: (1) commercial powder; (2) sieved powder  $d_p < 315 \mu\text{m}$ ; (3) sieved powder  $d_p > 315 \mu\text{m}$ .

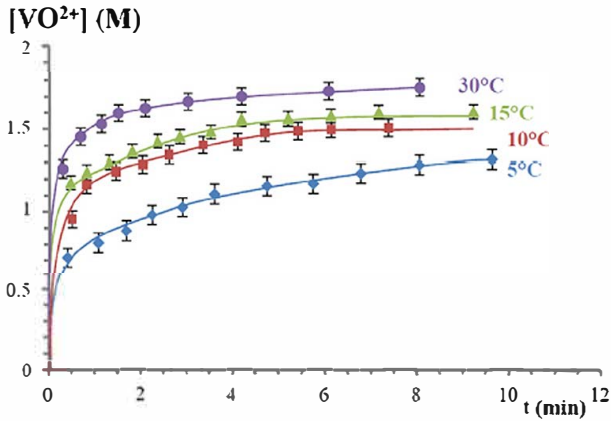


Fig. 3. Temporal evolution of the concentration of  $\text{VO}^{2+}$  released by the dissolution of a  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  commercial powder, for various temperatures;  $[\text{H}_2\text{SO}_4] = 3 \text{ M}$ ; stirring 500 rpm; aliquots filtered by 0.23 and 0.1  $\mu\text{m}$  filters.

The first concentration reported on the graph corresponds to 20 s after the introduction of the solid into the stirred solution. For this first measurement, at 5 °C the vanadium concentration reaches 0.7 M and this value doubles (1.3 M) at 30 °C.

The concentration of the  $\text{VO}^{2+}$  measured at 20 s, will be used to determine the initial dissolution rate  $r^0$  (defined as the ratio  $\frac{[\text{VO}^{2+}]_{20\text{s}}}{20\text{s}}$ ). Assuming that the kinetic constant of the initial dissolution rate follows the Arrhenius law, Eq. (1) gives the initial dissolution rate  $r^0$ .

$$r^0 = k \times f = A \times e^{-E_a/RT} \times f \quad (1)$$

where  $f$  is a function of the various operating parameters (activity of the solid vanadyl sulfate, diffusion coefficient of  $\text{VO}^{2+}$ , size of solid particles. . .). Some of these parameters depend on the temperature and this dependence is expected to be studied in a future work. Here, in order to get a rough order of the magnitude of the activation energy, the experimental data were analyzed (assuming the function  $f$  independent of  $T$ ) and leads to the following linear regression:

$$\ln r^0 \left( \frac{\text{M}}{\text{s}} \right) = \frac{2266.7}{T(\text{K})} + 4.8579 \quad (2)$$

This relation leads to an approximation of the activation energy of 18.8 kJ/mol for the dissolution of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  in 3 M sulfuric acid, a value relatively low compared to the activation energy of a classical chemical reaction.

### 3.1.3. Effect of stirring rate and particle size on dissolution kinetics

Several dissolution experiments were achieved by applying three stirring rates (500, 100 and 15 rpm), corresponding respectively to (i) a well stirred homogeneous suspension, (ii) a minimum stirring rate enabling to uplift the particle and (iii) partially decanted solid. Besides, these experiments were carried out for two different particles size  $d_p$  ( $<315 \mu\text{m}$  and  $>315 \mu\text{m}$ ). The corresponding time evolution of  $\text{VO}^{2+}$  concentration is presented in Fig. 4.

For a defined range of particles size ( $d_p < 315 \mu\text{m}$  curves 1 2 3 or  $d_p > 315 \mu\text{m}$  curves 4 5 6, Fig. 4), it appears that a higher stirring rate increases the dissolution kinetics, since higher concentrations are achieved in a shorter time. For instance,  $[\text{VO}^{2+}]_{(d_p < 315 \mu\text{m}; \omega = 500 \text{ rpm}; t = 1')} = 1.5 \text{ M}$  and  $[\text{VO}^{2+}]_{(d_p < 315 \mu\text{m}; \omega = 100 \text{ rpm}; t = 1')} = 1.0 \text{ M}$ .

Under constant stirring, the dissolution rate increases by decreasing the particles size. Thus, for a given dissolution time, and before reaching equilibrium, higher salt concentrations were measured with smaller particles. Indeed comparison of curves (1) and (4) obtained in two "well stirred" suspensions show that the concentration of  $\text{VO}^{2+}$  after 1 min reaction time increases from  $\sim 1.2$  to  $\sim 1.5 \text{ M}$  when the size decreases from  $d_p > 315 \mu\text{m}$  to  $d_p < 315 \mu\text{m}$ .

A different shape is obtained for curves (3) and (6), which corresponds to the lowest stirring rate; they exhibit the slowest dissolution rate for both particle sizes. The slow agitation does not enable the motion of the particles which sediment at the bottom of the vessel, forming a 'coagulated' powder paste. Around each grain of this paste, the  $\text{VO}^{2+}$  concentration reaches rapidly the saturation concentration. These facts are in agreement with a dissolution rate limited by mass transfer. For long reaction time, all the curves tend to converge to the same saturation concentration ( $\sim 1.7$  to  $1.8 \text{ M}$ ).

### 3.1.4. Equilibrium data

After a certain time of stirring (between 5 and 10 min), the solution is saturated and the concentration of  $\text{VO}^{2+}$  is constant. The equilibrium values are reported in Fig. 5, along with data from Skyllas Kazacos et al. (2016) and Rahman and Skyllas Kazacos (1998).

A satisfactory agreement is observed between our results and those of previous works, which confirms that the solubility of  $\text{VO}^{2+}$  increases with temperature. For the highest comparable temperature (30 °C), a significant difference of around 20% is observed.

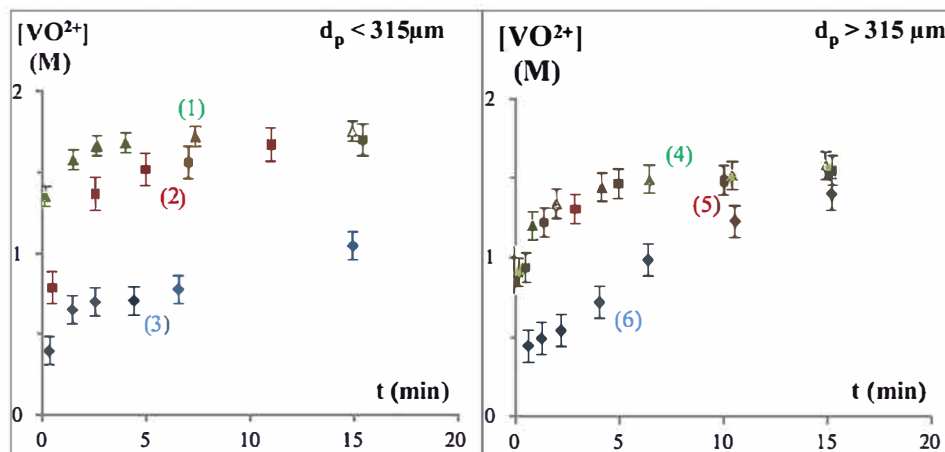


Fig. 4. Temporal evolution of the concentration of  $\text{VO}^{2+}$  released by the dissolution of a  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  commercial powder, for suspensions containing two different particle sizes and subjected to various stirring rates  $\omega$ .  $T = 25 \text{ }^\circ\text{C}$ ,  $[\text{H}_2\text{SO}_4] = 3 \text{ M}$ ,  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  powder; Left:  $d_p < 315 \mu\text{m}$ :  $\omega$  (in rpm) for (1), (2) and (3) are 500/triangles, 100/squares and 15/diamonds respectively; Right:  $d_p > 315 \mu\text{m}$ :  $\omega$  (in rpm) for (4), (5) and (6) are 500/triangles, 100/squares and 15/diamonds respectively.

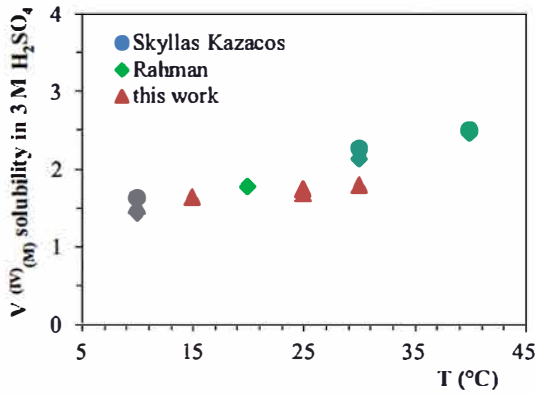


Fig. 5. Influence of temperature on the solubility of  $V^{(IV)}$ . Triangles: this work; circles: M. Skyllas-Kazacos et al.; diamonds: F. Rahman et al.

This could be attributed to the difficulties encountered in the measurement of a precise volume at this temperature.

The results show that the solubility of  $VO^{2+}$  increases with temperature. The equilibrium constant of the  $VOSO_4 \cdot 5H_2O$  dissolution (reaction (3)) can be written as following:

$$K_{(3)} = \frac{(a_{VO^{2+}} \times a_{SO_4^{2-}})}{a_{VOSO_4 \text{ solid}}} \text{ at the equilibrium} \quad (3)$$

Even if the first dissociation of  $H_2SO_4$  to  $HSO_4^-$  is total (high  $K_{H_2SO_4/HSO_4^-}$ ), the second dissociation to  $SO_4^{2-}$  remains partial with an equilibrium constant  $K_{HSO_4^-/SO_4^{2-}} = 0.013$  at 25 °C (the concentrations are in mol/kg) (Wallace, 1966). However, the released quantity of sulfate ions from  $HSO_4^-$  dissociation is not significant compared to the quantity released from the dissolution of  $VOSO_4$ ; this imply that  $[VO^{2+}]$  can be assumed equal to  $[SO_4^{2-}]$ .

Concerning the activity of the solid powder of  $VOSO_4$ , we will assume it equal to 1. Thereby, the above equation can be written as follows:

$$K_{(3)} \frac{\gamma_{VO^{2+}} \times \gamma_{SO_4^{2-}}}{a_{VOSO_4 \text{ solid}}} \times [VO^{2+}] \times [SO_4^{2-}] \Rightarrow K_{(3)} \lambda \times \left( [VO^{2+}]_{\text{at equilibrium}} \right)^2 \quad (4)$$

$$\text{where } \lambda = \frac{\gamma_{VO^{2+}} \times \gamma_{SO_4^{2-}}}{a_{VOSO_4 \text{ solid}}}$$

Because the concentrations of  $VO^{2+}$  at saturation are relatively high (1.2–1.7 M), the activity coefficients depend on the concentration, while the activity of the vanadyl sulfate solid is equal to 1; in a future work, the Pitzer model will be used in order to express these activity coefficients. Here, in order to get a rough estimation of the sensitivity of vanadyl sulfate solubility against temperature, the logarithm of the  $VO^{2+}$  saturation concentration was plotted versus  $1/T$ , assuming  $\lambda$  independent from the concentration of the various species.

The linear regression analysis leads to the following relation:

$$\ln[VO^{2+}]_{\text{sat (mM)}} = \frac{982.2}{T(\text{inK})} + 3.8$$

with a relatively low correlation coefficient ( $R^2 = 0.91$ ) with the experimental results, explaining the uncertainties due to the dependence of the activity coefficients on the concentration.

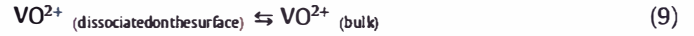
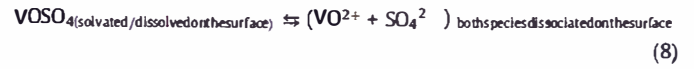
From the slope of the above equation ( $982.2 \text{ kJ}/(2R)$ ), we deduce the value of  $k = 16.3 \text{ kJ/mol}$ .

The obtained value is (i) positive showing the endothermic character of the vanadyl sulfate dissolution, and (ii) a relatively low value, compatible with the dissociation of an ionic salt weakly bonded.

### 3.1.5. Elucidation of the mechanism of the vanadyl sulfate dissolution

The results of this study show that, at constant temperature, the dissolution of vanadyl sulfate in 3 M sulfuric acid is limited by mass transport and that two main parameters (stirring rate and particle size) affect the dissolution rate.

Let us consider the following mechanism for the dissolution of the solid salt  $VOSO_4 \cdot 5H_2O$ :



Taking into account the results related to the effect of stirring (§3.1.3), the limiting step in the vanadyl sulfate dissolution will be assumed to be the transport of the  $VO^{2+}$  from the surface of the particles to the bulk i.e. reaction (9). Besides, in the absence of an electric field, the transport of ions produced in reaction (8) is assumed to occur both by diffusion and by convection.

The mass balance for  $VO^{2+}$  in the area between the surface of the particle and the bulk could be written, (using  $m$  as the  $V^{(IV)}$  molar concentration), as following:

Dissolution flux<sub>(7)</sub>  $\approx$  dissociation flux<sub>(8)</sub>  $\approx$  diffusion flux<sub>(9)</sub> = accumulation of  $VO^{2+}$  flux into the bulk

$$\left( \frac{\partial m}{\partial t} \right)_{\text{bulk}} = S \times D \times (\text{grad } \bar{C})_{\text{surface of particle}} \quad (\text{Fick's 1st law}) \quad (5)$$

To simplify, the  $VOSO_4 \cdot 5H_2O$  solid particles are considered spherical and a simple film model around the particle is creating the limitation to mass transfer (i.e. one direction transfer), the previous equation can be simplified as following:

$$\left( \frac{\partial m}{\partial t} \right)_{\text{bulk}} = S \times D \times \left( \frac{\partial \bar{C}}{\partial R} \right)_{\text{surface of particle}} \Rightarrow S \times k_{(t)} \times (C_{\text{sat}} - C_{\text{bulk}}) \quad (6)$$

The effect of the convection was examined on the mass transfer coefficient  $k_{(t)}$ , using the expression of Ranz and Marshall relative to a forced convection around a solid sphere (Cussler, 1984) (also known as the Leveque correlation providing the Sherwood number),

$$Sh \text{ Sherwood number} = \frac{k_{(t)} \times d_p}{D} = 2 + a \times Re^{1/2} \times Sc^{1/3} \quad (7)$$

This correlation is appropriated for spherical particles having the same size. In order to improve its applicability on the present case, some assumptions will be considered:

The calculations will be achieved assuming the presence of four separated size ranges of the solid particles having an initial radius  $R^0 = 20, 40, 500$  and  $1000 \mu\text{m}$  representing respectively 20%, 35%, 35% and 10% of the total solid volume (see curve of Fig. 2 1, cumulated volume);

All the particles of the powder will be assumed spherical, despite the various shapes observed (Fig. 1). Considering Eq. (7), the constant "a" is generally assumed equal to 0.6. However, in the present study and because of the large size distribution, "a" will be taken as an adjusting factor, which effect will be examined.

The molar quantity of the dissolved  $VO^{2+}$  "m" for N particles of initial radius  $R^0$  can be expressed as:



$$m \frac{\rho \times V}{M} = N \times V_{\text{one particle}} \times \frac{\rho}{M} \quad (8)$$

$$N \times \frac{4}{3} \pi \times (R^3 - R(t)^3) \times \frac{\rho}{M}$$

(Refer to notation and symbols)

The concentration of  $\text{VO}^{2+}$  in solution can be written as  $C_{\text{bulk}} = \frac{m}{V_l}$ ;  $V_l$  being the total volume of the suspension (including both the liquid and the solid).

Combining Eqs. (6)–(8) leads to Eq. (9) describing the variation of the radius  $R$  of the solid particles as a function of time, and representing the dissolution rate  $\dot{R}$  of the vanadyl sulfate:

$$\dot{R} = \frac{A_1 A_2 (R^3 - R(t)^3) + A_3 \sqrt{R(t)} A_4 (R^3 - R(t)^3) \sqrt{R(t)}}{R(t)} \quad (9)$$

where  $A_1$  to  $A_4$  are constants (refer to Appendix A for their developed expressions).

Eq. (9), written as  $\dot{R} = \frac{dR}{dt} = f(R)$ , is solved numerically using the Euler method ( $R_{j+1} = R_j + \text{step} \times f(R, t)$ ) and enables to calculate a theoretical radius at time  $t$ , given that at  $t^0 = 0$ ,  $R = R^0$ .

Note that the step used is:  $\frac{\text{reaction time}}{\text{number of iterations}} = \frac{10}{100} = 0.1 \text{ min}$

The value of the radius  $R$  of a certain particle of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ , obtained at a certain time  $t$ , from the resolution of Eq. (9) enables to obtain the theoretical values of the dissolved quantity of  $\text{VO}^{2+}$  i.e. the moles number, using Eq. (8).

Note that Eq. (9) is resolved 4 times, each for one of the chosen initial  $R^0$  (20, 40, 500 and 1000  $\mu\text{m}$ ) of the solid particles and the total concentration of the dissolved vanadium sulfate ( $\text{VO}^{2+}$ ) in solution is deduced (sum of the four obtained values of molar quantity divided by  $V_l$ ). Also, for each  $R^0$ , a different value of the adjusting factor “ $a$ ” (Eq. (7)) was determined.

Fig. 6 shows two examples of the iterative determination, at 30 °C, of the optimal value of two parameters (the constant “ $a$ ” in the Leveque equation and the percentage of each particle size range which directly affects the number of total particles  $N$  of each  $R^0$ ). The optimized value of “ $a$ ” or “ $N$ ”, is the one leading to a curve of the concentration of the dissolved vanadium sulfate which fits best with the experimental data curve.

Following this iterative mode enables to evaluate the calculated curves at each temperature and the results are presented in Fig. 7 comparatively to the experimental data. Note that the viscosity was calculated for each temperature (Fassulo, 1965), while the value of the diffusivity at 25 °C (Jiang et al., 2016) was used for all the examined temperatures.

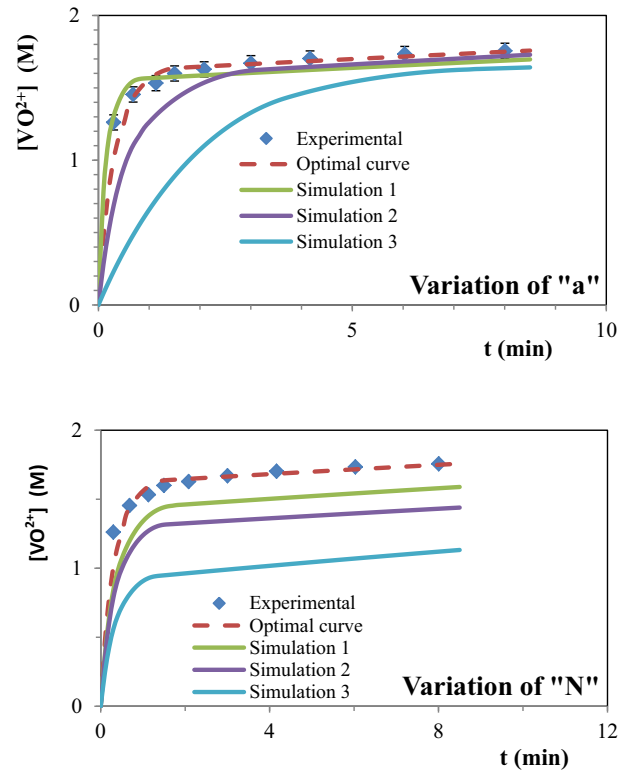
A relatively good agreement ( $\frac{\Delta C}{C} \pm 0.1 \text{ M} / \sim 1.5 \text{ M}$ ) is observed between the results of the model and the experimental ones. Discrepancies are observed for short durations of the dissolution ( $t < 1 \text{ min}$ ) because of the difficulty to standardize rapidly the suspension and to achieve precise measurement at the first few seconds after the stirring begins

Another difficulty comes from the dissolution of the smallest particles, which exhibit fast kinetics. In fact, compared to the bigger particles, this introduces additional uncertainties because the number of small particles of powder was not exactly taken into account.

To sum up, the obtained results lead to the following conclusions:

Regarding the effect of temperature:

- The initial dissolution rate increases with temperature.
- The solubility of the vanadyl sulfate at saturation (when the equilibrium of dissolution is reached) increases slightly with the temperature in the examined range of 5–30 °C, and this is compatible with the dissociation of an ionic salt weakly bonded.



**Fig. 6.** Temporal evolution of the concentration of  $\text{VO}^{2+}$  released by the dissolution of the  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  commercial powder: dots = experimental curves; Continuous lines = simulated curves obtained with the non optimized parameter value, i.e. the constant “ $a$ ” in the Leveque equation (figure on the top), and the percentage of each particle size range which directly affects the number of total particles “ $N$ ” of each  $R^0$  (figure on the bottom); Broken lines = simulated curves obtained with the optimized parameters of “ $a$ ” (figure on the top), and “ $N$ ” (figure on the bottom).

Both the stirring of the suspension and the size of the particles strongly affect the dissolution rate (mainly for dissolution times lower than 5 min), proving that the dissolution kinetics of the vanadyl sulfate (to  $\text{VO}^{2+}$ ), is limited by the mass transfer of  $\text{VO}^{2+}$  from the solid powder surface to the bulk, while the chemical reaction with the proton is not limiting.

### 3.2. Dissolution of vanadium pentoxide

#### 3.2.1. Characterization of the initial powder

The commercial powder of  $\text{V}_2\text{O}_5$  was characterized by SEM and laser diffraction particle sizing technique. The SEM micrograph in Fig. 8 1 shows that the  $\text{V}_2\text{O}_5$  particles form agglomerated sticks of various sizes. The size distribution (Fig. 8 2) shows a large dispersion of particle size from 120 nm to 4 mm.

The graph exhibits three peaks located respectively at 2, 80 and 900  $\mu\text{m}$ ; therefore, in order to study the effect of particles size on the dissolution kinetic, the initial powder was sieved using four different cut off threshold sieves: 315  $\mu\text{m}$ ; 200  $\mu\text{m}$ ; 120  $\mu\text{m}$  and 80  $\mu\text{m}$ . Thus, five different diameter ranges of powder were obtained:  $d_p > 315 \mu\text{m}$ ;  $315 > d_p (\mu\text{m}) > 200$ ;  $200 > d_p (\mu\text{m}) > 120$ ;  $120 > d_p (\mu\text{m}) > 80$  and  $d_p (\mu\text{m}) < 80$ , three of which were used to carry out dissolution experiments.

#### 3.2.2. Effect of temperature on dissolution kinetics

The effect of temperature on the dissolution of vanadium pentoxide was studied in the range 0–40 °C and the temporal evolution of the dissolved  $\text{VO}_2^+$  concentration is presented in Fig. 9.

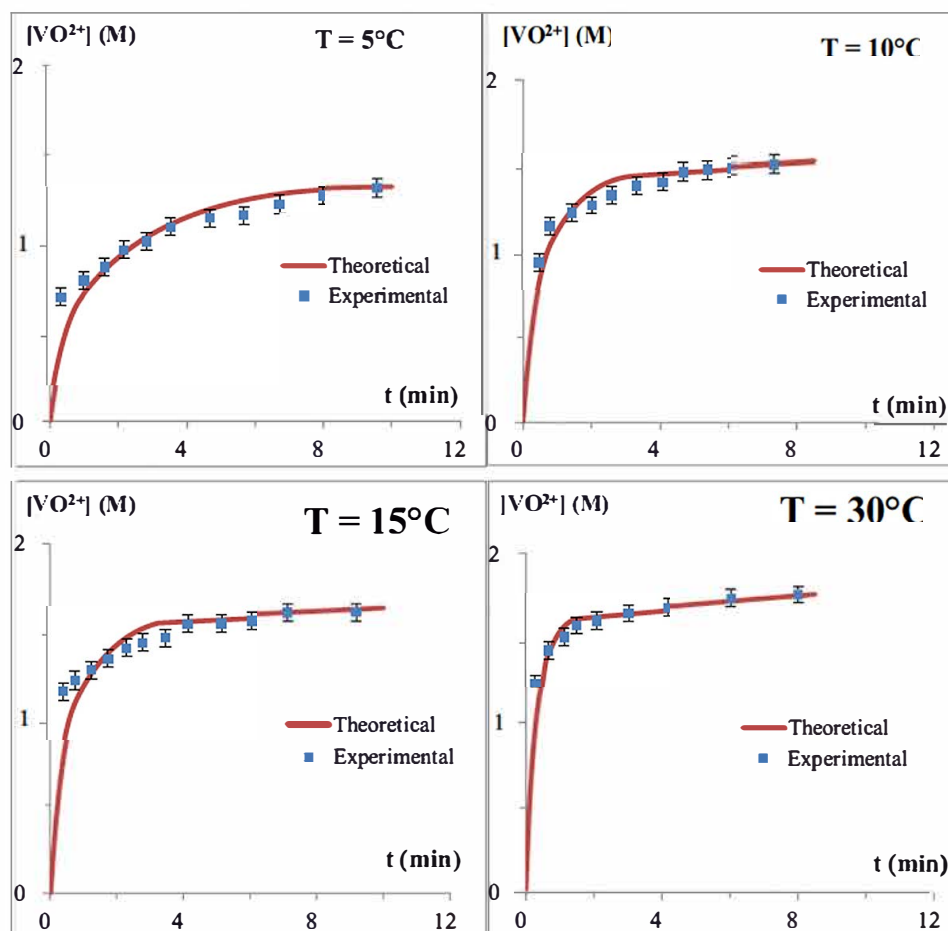


Fig. 7. Comparison between the experimental data (reported from Fig. 3) and the model (calculated using Eq. (9)) of the temporal evolution of the concentration of  $\text{VO}_2^+$  released by the dissolution of a  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  commercial powder, at various temperatures.

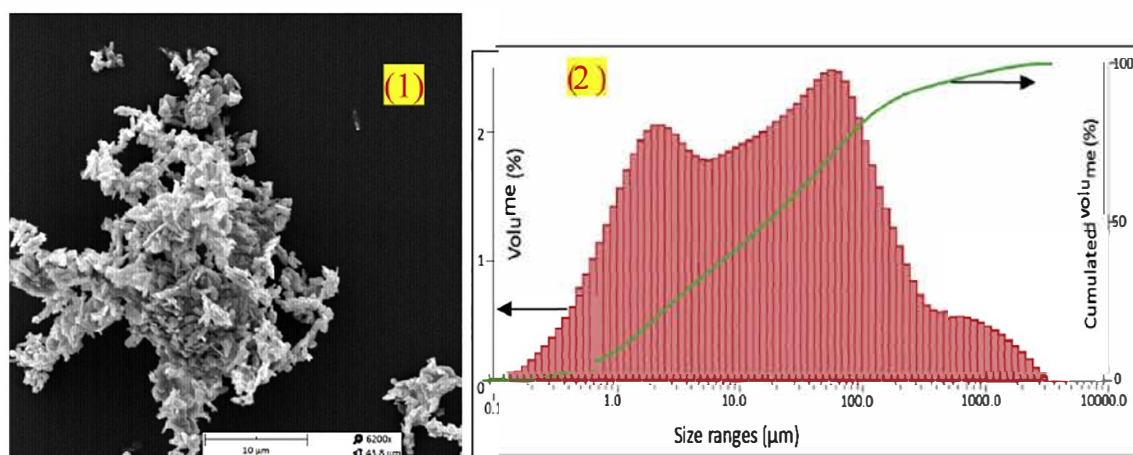


Fig. 8. (1) SEM pictures (10 kV-Point, SED) and (2) size distribution obtained (by laser diffraction sizing technique: P = 3 bar, dry mode) of the vanadium pentoxide  $\text{V}_2\text{O}_5$  commercial powder.

The behavior is rather similar for each temperature: a rapid dissolution occurs at "short" reaction times (less than 1 h) and then the concentration tends to reach a constant value. Note that, for all the examined temperatures (except 0 °C), the dissolution equilibria of the vanadium pentoxide to  $\text{VO}_2^+$  is achieved after 5 h of

stirring; for the dissolution at 0 °C a higher reaction time is required to reach the saturation.

Several differences can be observed compared to the dissolution features of  $\text{VOSO}_4$ :

The saturation concentrations ( $C_{sat}$ ) of  $VO_2^+$  are about three times lower than those of the  $VO_2^{2+}$ ; in addition, the  $C_{sat}$  decreases when the temperature increases (contrary to the case of the  $V^{(IV)}$ , where  $C_{sat}$  increases with  $T$ ). This point will be analyzed in the next section.

For the stronger stirring (500 rpm), the time required to dissolve the oxide and to reach the saturation concentration of  $VO_2^+$  is more than fifty times higher than that required for the  $VO_2^{2+}$ . Typical comparative values are 5 min to reach a concentration of  $VO_2^{2+}$  of 1.5 M, while 3 h were required to reach a concentration of  $VO_2^+$  of 0.5 M. Moreover, at 40 °C, the saturation concentration of  $VO_2^+$  is reached for  $t < 20$  min, while at 0 °C the solution is not saturated, even after 5 h. Another experiment was carried out at 0 °C where the suspension of vanadium pentoxide was left under stirring for one day. The concentration of the dissolved  $VO_2^+$  was determined and the following values were obtained:  $[VO_2^+]_{23h} = 0.788$  M and  $[VO_2^+]_{25h} = 0.783$  M. This last result tends to show that the mass transport is not the limiting step.

The concentration of the  $VO_2^+$  measured for reaction times lower than five minutes (named  $t_{initial}$ ), will be used to estimate approximately the initial rate of the  $V_2O_5$  dissolution  $r^0$  (defined as the ratio  $\frac{[VO_2^+]_{t_{initial}}}{t_{initial}}$ ).

Assuming, as for the vanadyl sulfate, that (i) the kinetic constant of the initial dissolution rate follows the Arrhenius law, and (ii) the others terms of the expression of the dissolution rate are independent of the temperature, then, the logarithmic analysis of the evolution of the initial rate with the temperature leads to the following correlation:

$$\ln r^0_{(r^0 \text{ in } \frac{M}{h})} = 22.7 \frac{8727.3}{T_{(in \text{ } K)}} \quad (10)$$

The slope of this linear relation enables the determination of a roughly estimated value of the activation energy of the dissolution process:  $E_a = 73$  kJ/mol.

This energy is more than four times higher than the value obtained for the dissolution of  $VOSO_4$  (18.8 kJ/mol). This could be explained by the fact that the hydration of the vanadium pentoxide ( $V_2O_5$  which exhibits covalent bonds) followed by its reaction with  $H^+$  ions is energetically more difficult to achieve, comparatively to the simple dissociation of the ionic salt  $VOSO_4$ .

### 3.2.3. Effect of available surface area on dissolution kinetics

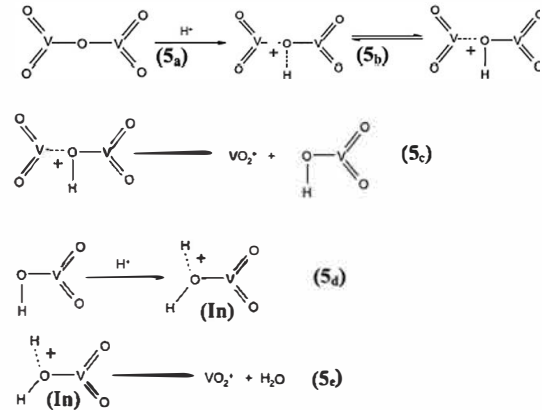
The effect of the particle size on the dissolution rate of  $V_2O_5$  was examined at 40 °C and 500 rpm stirring rate and the results are shown in Fig. 10.

Practically the same concentrations were measured for the three different size ranges of the solid particles ( $80 < d_p < 120 \mu m$ ,  $120 < d_p < 200 \mu m$  and  $200 < d_p < 315 \mu m$ ). These results tend to show that the dissolution rate does not depend on the solid/liquid exchange surface. Theoretically, the particle size affects the initial rate of the dissolution that should increase. However, in our case, owing to the low values of these dissolution rates, the curves do not have enough resolution to show any difference. Moreover, these results support our previous conclusion: the mass transfer does not represent a limitation to the dissolution of  $V_2O_5$  but it is rather the chemistry of the system.

Consequently, the effect of stirring on the dissolution was not studied.

Since the dissolution is not significantly affected by the particles size, the possibility of kinetic control by surface passivation was evaluated.

A simplified reaction scheme is proposed below for the vanadium pentoxide dissolution (R5):



Hydrogen ion attacks the oxide and the product obtained from reaction (5b) decomposes according to reaction (5c); then by reaction with  $H^+$ , it forms an intermediate (In) which dehydrates to lead to  $VO_2^+$ .

However, another reaction pursue of the intermediate (In) could be its polymerization according to various reactions and in the last case, the external surface of each solid particle could be entirely covered by a passive layer that prevents the dissolution and could be the reason for which the observed saturation concentration of  $VO_2^+$  remains low.

To clarify this point, the following dissolution experiment was carried out: a solid liquid suspension of the commercial  $V_2O_5$  sieved powder ( $200 < d_p < 315 \mu m$ ) was introduced into a  $H_2SO_4$  3 M solution at 25 °C and stirred during 5 h. The results are illustrated in Fig. 11: the  $[VO_2^+]$  increases to reach the saturation concentration ( $\sim 0.55$  M after  $t \sim 1$  h) then remains constant. Then the suspension was filtered to remove the residual solid and a fresh sample of the powder was added into the filtrate. The dissolution experiment was pursued for 6 h, and the temporal evolution of the concentration of the vanadium is indicated into Fig. 11 (for  $t > 22$  h until  $t = 28$  h). The renewal of the solid does not change the dissolved amount of vanadium, implying that the equilibrium was reached and no further dissolution can be achieved. This test confirms that there is no passivating or inhibiting layer formed on the surface of the particles.

### 3.2.4. Equilibrium data

The saturation concentration of  $VO_2^+$ , obtained for  $t > 5$  h (extracted from Fig. 9), are reported in Fig. 12, simultaneously with the values from Rahman (1998), Skyllas Kazacos et al. (2016). Note that the values extracted from the bibliography were multiplied by 2 in order to obtain the concentration of  $VO_2^+$ , instead of the solubility of  $V_2O_5$  used in the cited references. The saturation concentration of  $VO_2^+$  decreases when the applied temperature increases, even if a shorter time is required to reach the equilibrium.

The equilibrium constant of reaction (5) can be written as a function of the activities of the species in solution:

$$K_{(5)} = \frac{(a_{VO_2^+})^2 \times a_{H_2O}}{a_{V_2O_5 \text{ solid}} \times (a_{H^+})^2} = \frac{a_{H_2O} \times (\gamma_{VO_2^+})^2}{a_{V_2O_5 \text{ solid}} \times (\gamma_{H^+})^2} \times \left( \frac{[VO_2^+]}{[H^+]^0} \right)^2 \quad (11)$$

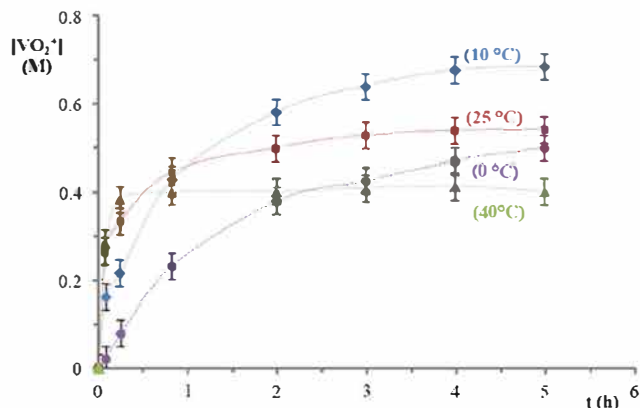


Fig. 9. Temporal evolutions of the concentration of the  $\text{VO}_2^+$  (released by the dissolution of a  $\text{V}_2\text{O}_5$  commercial powder), at various temperatures;  $[\text{H}_2\text{SO}_4] = 3 \text{ M}$ ; stirring 500 rpm.

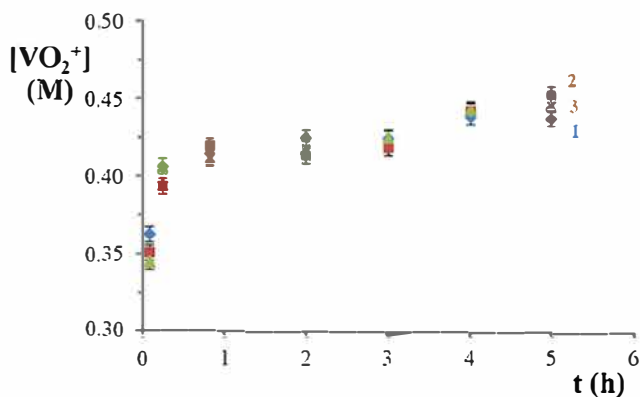


Fig. 10. Temporal evolutions of the dissolved  $\text{VO}_2^+$  concentration (released by the dissolution of a  $\text{V}_2\text{O}_5$  commercial powder) for various initial sizes of the solid particles of  $\text{V}_2\text{O}_5$  obtained by sieving;  $[\text{H}_2\text{SO}_4] = 3 \text{ M}$ , stirring 500 rpm, sieved  $\text{V}_2\text{O}_5$  powder,  $T = 40 \text{ }^\circ\text{C}$ . (1)  $80 < d_p < 120 \text{ } \mu\text{m}$ ; (2)  $120 < d_p < 200 \text{ } \mu\text{m}$ ; (3)  $200 < d_p < 315 \text{ } \mu\text{m}$ .

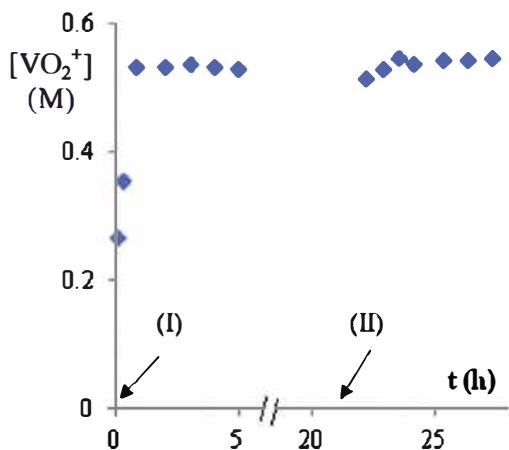


Fig. 11. Temporal evolution of the  $\text{VO}_2^+$  concentration (released by the dissolution of a  $\text{V}_2\text{O}_5$  commercial powder) for two different additions of solid samples of  $\text{V}_2\text{O}_5$  into the liquid;  $15 \text{ cm}^3$  of  $[\text{H}_2\text{SO}_4] = 3 \text{ M}$ , stirring 500 rpm,  $T = 25 \text{ }^\circ\text{C}$ , sieved  $\text{V}_2\text{O}_5$  powder ( $200 < d_p < 315 \text{ } \mu\text{m}$ ). (I) first introduction of 2.2 g of  $\text{V}_2\text{O}_5$ ; (II) filtration and second introduction of 2.2 g of  $\text{V}_2\text{O}_5$ .

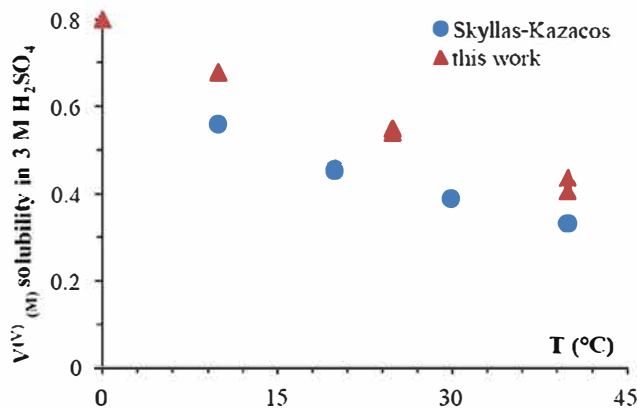


Fig. 12. Influence of temperature on the solubility of  $\text{V}^{(V)}$ . Triangles: this work; circles: Rahman (1998), Skyllas-Kazacos et al. (2016).

In the present case, the concentrations of the  $\text{VO}_2^+$  at saturation are lower than the values obtained for  $\text{VO}^{2+}$  at saturation (Fig. 9: 0.4–0.7 M for stirring duration of 5 h). The effect of the concentration on the activity coefficient will also be examined in a future work via the Pitzer model.

For the time being, in order to get a preliminary rough estimation of the sensitivity of the vanadium pentoxide solubility against

the temperature, the term  $\frac{a_{\text{H}_2\text{O}} \times (\gamma_{\text{VO}_2^+})^2}{a_{\text{V}_2\text{O}_5 \text{ solid}} \times (\gamma_{\text{H}^+})^2}$  will be considered constant and named  $\xi$ . Then a logarithmic analysis of the data at the equilibrium (Fig. 9) versus the reverse temperature was performed according to the following equation:

$$\ln \left( \frac{[\text{VO}_2^+]_{\text{sat}}}{[\text{H}^+]^0 [\text{VO}_2^+]_{\text{sat}}} \right) = 0.5 \times (\text{constant} \ln \xi) \frac{k'}{2R} \times \frac{1}{T} \quad (12)$$

The linear regression analysis of the experimental results leads to the following equation  $\ln \left( \frac{[\text{VO}_2^+]_{\text{sat}}}{[\text{H}^+]^0 [\text{VO}_2^+]_{\text{sat}}} \right) = 9.15 + \frac{2272}{T}$  with a correlation coefficient with the experimental results of  $R^2 = 0.9997$ , a satisfactory value taking into account the uncertainties on the dependence of the activity coefficient to the concentration.

The slope of the above equation ( $+2272 \text{ k}'/(2R)$ ), enables to deduce  $k' = -37.8 \text{ kJ/mol}$ , a negative value; it could be attributed, very approximately, to the changes in the enthalpy of the reaction between  $\text{H}^+$  and  $\text{V}_2\text{O}_5$  which appears to be an exothermic process. This is also confirmed by the bibliography and particularly the studies of (Rahman and Skyllas Kazacos, 2009) which claims that the reaction (5) is an endothermic reaction. Note that, the obtained negative value is in agreement with the effect of temperature on the saturation concentration: the saturation concentration of  $\text{VO}_2^+$  decreases when the temperature of the stirred suspension increases.

Besides comparison of  $k$  for the vanadyl sulfate ( $+16.3 \text{ kJ/mol}$ ) and  $k'$  for the vanadium pentoxide ( $-37.8 \text{ kJ/mol}$ ) enables to conclude that the dissolution of both vanadium compounds follows different schemes: the process is endothermic for the dissolution of  $\text{VOSO}_4$  and exothermic and more 'difficult' for the breaking of the oxide bonds ( $\text{V}-\text{O}$  bond have a more covalent character than bond  $\text{VO}-\text{SO}_4$  bond).

### 3.2.5. Kinetic model of the dissolution

The comparison of the dissolution of both  $\text{VOSO}_4$  and  $\text{V}_2\text{O}_5$  lead to the following conclusions:

The time required to saturate the solution with  $\text{VO}_2^+$  is in the order of "some hours" compared to a time in the order of some minutes for  $\text{VO}^{2+}$ , especially for 'low' temperature ( $0^\circ\text{C}$ ). Moreover, the saturation concentration of the  $\text{VO}_2^+$  is, as function of  $T$ , much lower than the saturation concentration of  $\text{VO}^{2+}$ ; Taking into account the fact that 5 h were required to saturate the  $\text{V}^{(V)}$  solution, it can be concluded that the mass transfer is not a limiting factor of the oxide dissolution. Besides, it was shown that the observed limitation in the  $\text{V}_2\text{O}_5$  dissolution does not come from the physical properties of the powder, nor from an eventual secondary reaction taking place on the particles' surface and blocking the main dissolution (§ 3.2.3).

Therefore, the dissolution of the  $\text{V}^{(V)}$  will be assumed to be limited by the chemistry of the reaction (5) assumed to be a slow equilibrium, of which the global rate can be expressed by the Eq. (13).



$$r_{(5)} = \frac{1}{2} \frac{d[\text{VO}_2^+]}{dt} = k_{f(5)} \times \left(\frac{N_{\sigma_i}}{N_a}\right)^\alpha \times \left(\frac{\text{moles of H}^+}{V_{\text{suspension}}}\right)^\beta \times \left(\frac{\text{moles of VO}_2^+}{V_{\text{suspension}}}\right)^\gamma \quad (13)$$

(Refer to Appendix B for the detailed development of Eq. (13)) Thus, for particles 'i' having, at the time t:

$S_i$  as surface  
 $N_{\sigma_i}$  sites on their surface, and  
releasing by dissolution  $2(X)_{S_i}$  moles of  $\text{VO}_2^+$

The dissolution rate Eq. (13) can be expressed as following:

$$r_{(5)S_i} = \frac{1}{2} \frac{d[\text{VO}_2^+]_{S_i}}{dt} = \frac{1}{2} \frac{d(2X)_{S_i}}{V_{\text{suspension}} dt} = \frac{d(X)_{S_i}}{V_{\text{suspension}} dt} = k_{f(5)} \times \left(\frac{N_{\sigma_i}}{N_a}\right)^\alpha \times \frac{\left\{n^{\circ\text{H}} \cdot 2 \times (X)_{S_i}\right\}^\beta}{V_{\text{suspension}}^\beta} \times k_{r(5)} \frac{\left\{2 \times (X)_{S_i}\right\}^\gamma}{V_{\text{suspension}}^\gamma} \quad (14)$$

The same equation will be written three times, because for the calculation, three particle surfaces  $S_1$ ,  $S_2$  and  $S_3$  are considered relatively to three particle diameters: 10, 60 and 1000  $\mu\text{m}$  according to the Fig. 8 2.

Then the resolution of each equation will provide the released moles number  $(2X)_{S_i}$  of  $\text{VO}_2^+$ , and in order to determine the global released moles number of  $\text{VO}_2^+$ , it is necessary to sum the four individual moles numbers, i.e.  $(2X)_{\text{global}} = (2X)_{S_1} + (2X)_{S_2} + (2X)_{S_3}$ .

On the other hand, the expression of  $N_{\sigma}$ , considered to be the number of available  $\text{V}_2\text{O}_5$  sites, as a function of the particle radius  $R_i$  and the vanadium initial concentration can be written as:

$$N_{\sigma_i} = \frac{N_i}{\sigma^\circ} \times \left(\frac{3(4\pi)^{0.5} M}{\rho}\right)^{2/3} \times (n^{\circ\text{V}} \cdot X_{R_i})^{2/3}$$

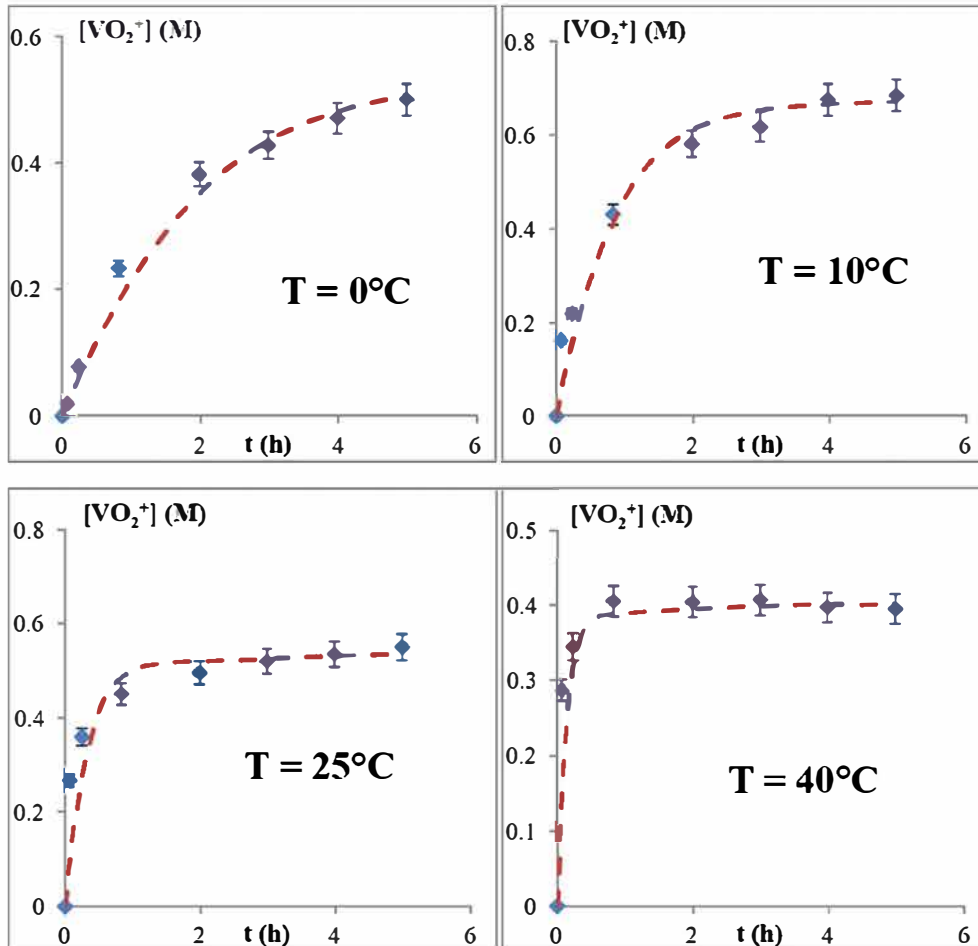


Fig. 13. Comparison between the experimental data (diamonds, imported from Fig. 9) and the model (broken lines, calculated using Eq. (15)) for the temporal evolution of the concentration of  $\text{VO}_2^+$  released by the dissolution of a  $\text{V}_2\text{O}_5$  commercial powder, at various temperatures.

**Table 1**

Iteratively estimated values of the kinetic constants  $k_{(5)}$  and  $k_{(-5)}$  for the studied temperatures, and their corresponding activation energies (estimations).

Temperature (°C)	$k_{(5)}$ (mol <sup>-2</sup> s <sup>-1</sup> L g)	$k_{(-5)}$ (mol <sup>-1</sup> s <sup>-1</sup> L)
0	$0.9 \times 10^{-4}$	$2.3 \times 10^{-4}$
10	$2.6 \times 10^{-4}$	$3.4 \times 10^{-4}$
25	$4.8 \times 10^{-4}$	$13 \times 10^{-4}$
40	$7 \times 10^{-4}$	$41 \times 10^{-4}$
Activation energy (estimated by $k = Ae^{E_a/RT}$ )	$E_a$ (5) = 34.5 kJ/mol	$E_a$ (-5) = 52.9 kJ/mol

Substituting it in Eq. (14) and considering the reaction orders with respect to  $V_2O_5$ ,  $H^+$  and  $VO_2^+$ , to be equal to their stoichiometric coefficients, the expression of global rate of the reaction is:

$$r_{(5)S_i} = \frac{d(X)_{S_i}}{dt} = k_{(5)} \times \frac{N_i}{N_a \times \sigma^\circ} \times \left( \frac{3(4\pi)^{0.5} M}{\rho} \right)^{2/3} \times (n^{\circ} V_{R_i})^{2/3} \times \frac{\left\{ n^{\circ} H \right\}^2 \times \left\{ 2 \times (X)_{S_i} \right\}^2}{V_{suspension}} \times k_{(-5)} \frac{\left\{ 2 \times (X)_{S_i} \right\}^2}{V_{suspension}} \quad (15)$$

Eq. (15), solved numerically using the Euler method, provides the variation of the quantity of  $VO_2^+$  as a function of time. The only unknown parameters are  $k_{(5)}$  and  $k_{(-5)}$ , the kinetic constants of the forward and backward reaction. They will be adjusted in order to determine the theoretical evolution of the  $VO_2^+$  concentration which correctly correlates with the experimental one.

Fig. 13 shows the correlation between the calculated values of dissolved  $VO_2^+$  (broken lines) and the experimental data (diamonds). The values of the kinetic constants, enabling to get a satisfactory agreement between theory and experiment, are indicated in Table 1.

The results show that the backward kinetic constant  $k_{(-5)}$  is more sensitive to the temperature than the forward  $k_{(5)}$ . Besides, for all the examined temperatures,  $k_{(-5)}$  is higher than the  $k_{(5)}$ . This means that the dissolution of the oxide is allowed only for 'relatively' low concentrations of  $VO_2^+$ , enabling to keep the term of the backward rate lower than this of the forward rate.

Note also that, because the order against the  $H^+$  concentration (in the forward term of the rate) is equal to 2, the acidic media is beneficial to the dissolution of the oxide and this is also in agreement with the results of Rahman and Skyllas Kazacos (2009).

#### 4. Conclusion

Numerous works exist in the field of the vanadium battery and one important objective is to avoid the vanadium pentoxide precipitation, because its dissolution seems difficult. In addition, the published studies do not exhibit the determination of the physical limitations and phenomena to be overcome, in order to act upstream. The aim of present work was the study of the dissolution mechanisms of the vanadyl sulfate  $VOSO_4$  and vanadium pentoxide  $V_2O_5$  in 3 M sulfuric acid, under various operative conditions, and also to bring knowledge on the understanding of the phenomena governing these dissolutions.

Several experimental data giving the temporal evolution of the dissolved vanadium concentrations versus various operating parameters were acquired and supplied. Moreover, kinetic laws describing both dissolution limitations phenomena were determined and explained. As expected these compounds exhibit different behaviors towards dissolution. The general results show that the dissolution of  $VOSO_4 \cdot 5H_2O$ , an 'ionic salt', appears to be easier

and more rapid, comparatively to that of the  $V_2O_5$  oxide (which is covalently bonded).

Their initial dissolution rate increases with temperature, for both compounds  $VOSO_4$  and  $V_2O_5$ , and the rough estimations of the activation energies at the beginning of the dissolution (18.8 kJ/mol for  $VOSO_4$  and 73 kJ/mol for  $V_2O_5$ ) clearly show that the temperature influence two different phenomena: the mass transport for the vanadyl sulfate, and the reaction with the proton for the vanadium pentoxide.

The saturation concentration of the  $VO^{2+}$  is reached after few minutes of stirring (<10 min), while several hours (>5h) were required for the  $VO_2^+$  released by the oxide  $V_2O_5$  to reach saturation (and more than 1 day at 0 °C). In addition the solubility of the  $V^{(IV)}$  salt is higher than the solubility of the oxide (at least two times, even three for certain temperatures):  $VO^{2+}$  concentrations of 2 M can be achieved from the dissolution of  $VOSO_4$  at  $T \geq 30$  °C, while for the oxide dissolution the  $VO_2^+$  saturation concentration reaches ~0.45 M at 40 °C.

Moreover, conversely to the  $V^{(IV)}$ , in the case of vanadium pentoxide decreasing the temperature causes the saturation concentration of  $VO_2^+$  to increase: from 0.42 to 0.78 M respectively at 40 and 0 °C, and the whole dissolution process appears to be exothermic ( $k' = 37.8$  kJ/mol).

Concerning the kinetic models, the dissolution of  $VOSO_4$  consists of the dissociation in the acid media, followed by its dispersion in the bulk. The whole process is limited by mass transport (more specifically diffusion and convection). The accumulation flux of  $VO^{2+}$  was expressed using Fick's 1<sup>st</sup> law and the Sherwood correlation and the simulated results enable to reproduce experimental measurements and to validate the mass transport limitation. For  $V_2O_5$ , the dissolution rate appears to be limited by a chemical reaction (acidic attack followed by the breaking bonds). A simple reaction scheme was proposed for the dissolution and its rate was expressed assuming the chemical reaction as an elementary reaction. The model agrees with the experimental data and the resulting kinetic constants show a backward reaction (-5) more sensitive to temperature and having a rate in certain conditions higher than the rate of the forward reaction (5).

Note that the obtained results were very sensitive to the sulfuric acid concentration which changes during the battery operation (increases during the charge and decreases during the discharge). The 3 M of sulfuric acid was chosen as a compromise between its positive effect on the dissolution of the vanadium pentoxide and its negative effect on the dissolution of vanadium sulfate.

To sum up, in the absence of chemical additives enabling to keep the  $V^{(V)}$  under dissolved form and avoid precipitation of the vanadium pentoxide, it is required to operate in strong acidic conditions, with a "discharged battery" instead of a "battery completely charged". Moreover, a charged vanadium battery will exhibit a more stable behavior if stored in low ( $T < 20$  °C) temperature conditions, rather than in high temperature conditions ( $T > 40$  °C). Also, taking into account the results of the bibliography, it is better to avoid maintaining the battery in recharged state for a long time.

#### Declaration of interests

The authors declare that there is no conflict of interest.

#### Acknowledgments

This study was supported by the Agence Nationale de la Recherche, France. The authors would like to acknowledge Brigitte Dustou, Laure Latapie and Sandrine Desclaux for the technical support they provided for the accomplishment of this work.

## Appendix A

The combination of Eqs. (6)–(8) enables to obtain the expression of  $\frac{dR}{dt}$  (Eq. (9)) also noted  $\dot{R}$  expressing the variation of the particles radius over time and representing the dissolution rate of the  $V_2O_5 \cdot 5H_2O$ . To reach this expression, the following calculation steps were followed:

$$Sh \frac{k(t) \times d_e}{D} \left( 2 + a \times Re^{\frac{1}{2}} \times Sc^{\frac{1}{3}} \right) \rightarrow k(t) \frac{D}{2R} \left( 2 + a \times Re^{\frac{1}{2}} \times Sc^{\frac{1}{3}} \right)$$

$$\left( \frac{dm}{dt} \right)_{R \rightarrow \infty} + S \times k(t) \times (C_{sat} - C_{bulk})$$

$$\frac{d \left( \frac{4}{3} \pi \times \frac{\rho \times N}{M} \times (R^3 - R_i^3) \right)}{dt} = 4\pi R^2 \times \left( \frac{D}{2R} \left( 2 + a \times Re^{\frac{1}{2}} \times Sc^{\frac{1}{3}} \right) \times \right.$$

$$\left. (C_{sat} - \frac{4}{3} \pi \times \frac{\rho \times N}{M \times V_l} \times (R^3 - R_i^3)) \right)$$

Developing the above equation leads to:

$$\frac{R \times dR}{dt} = \frac{MDC_{sat}}{\rho} - \frac{4}{3} \pi \frac{ND}{\rho V_l} (R^3 - R_i^3) + \frac{aMC_{sat}}{2\rho} (2 \times \frac{1}{6})^{\frac{1}{2}} D^{\frac{1}{2}} V_l^{-\frac{1}{6}} R^{\frac{1}{2}}$$

$$- \frac{4}{6} \pi \frac{aN}{V_l} (2 \times \frac{1}{6})^{\frac{1}{2}} D^{\frac{1}{2}} V_l^{-\frac{1}{6}} (R^3 - R_i^3) R^{\frac{1}{2}}$$

$$\dot{R} = \frac{dR}{dt} = \frac{A_1 - A_2 (R^3 - R_i^3) + A_3 \sqrt{R} - A_4 (R^3 - R_i^3) \sqrt{R}}{R} \quad (9)$$

$A_1$	$A_2$	$A_3$	$A_4$
$\frac{M \times D \times C_{sat}}{\rho}$	$\frac{4}{3} \pi \frac{D \times N}{V_l}$	$\frac{aMC_{sat}}{2\rho} (2 \times \frac{1}{6})^{\frac{1}{2}} D^{\frac{1}{2}} V_l^{-\frac{1}{6}}$	$\frac{4}{6} \pi \frac{aN}{V_l} (2 \times \frac{1}{6})^{\frac{1}{2}} D^{\frac{1}{2}} V_l^{-\frac{1}{6}}$

## Appendix B

$$r_{(5)S_i} = \frac{1}{2} \frac{d[VO_2^+]}{dt} \times k_{(5)} \times \left( \frac{N_{\sigma}}{N_a} \right)^{\alpha} \times \left( \frac{\text{moles of } H^+}{V_{suspension}} \right)^{\beta} \times k_{(5)} \times \left( \frac{\text{moles of } VO_2^+}{V_{suspension}} \right)^{\gamma} \quad (13)$$

The following nomenclature will be used to treat this equation and to determine the theoretical concentration of  $VO_2^+$ :

For the considered weight of the  $V_2O_5$  particles having as initial diameter: 10, 60 and 1000  $\mu\text{m}$  (from Fig. 8), it will be noted:

$S_1^{\circ}, S_2^{\circ},$  and  $S_3^{\circ}$ : their average initial surface.

$S_1, S_2$  and  $S_3$ : their average surface at the time  $t$ .

$R_1^{\circ}, R_2^{\circ}$  and  $R_3^{\circ}$ : their average initial radii.

$R_1, R_2$  and  $R_3$ : their average radii at the time  $t$ .

also:

$N_1, N_2$  and  $N_3$ : are the number of particles having as initial diameter: 10, 60 and 1000  $\mu\text{m}$

$N_{\sigma 1}, N_{\sigma 2}$  and  $N_{\sigma 3}$ : are the number of sites (i.e. the number of the  $V_2O_5$  molecules) accessible to the proton  $H^+$ , at time  $t$  for the particles having as initial diameter: 10, 60 and 1000  $\mu\text{m}$

$\sigma^{\circ}$ : is the surface occupied by one molecule of  $V_2O_5$

$N_a$ : Avogadro number

the exponents  $\alpha, \beta$  and  $\gamma$  are the reaction orders, respectively for a site constituted by  $V_2O_5, H^+$  and  $VO_2^+$ ;

$k_{(5)}$  and  $k_{(5)}$  the forward and backward kinetic constants respectively.

$N_{\sigma}$  = the number of sites accessible to  $H^+$ , at time  $t$   
 $= N_{\sigma 1} + N_{\sigma 2} + N_{\sigma 3} \frac{\text{surface of the particles at the time } t}{\text{surface occupied by one molecule}} \frac{\Sigma(N_j \times S_j)}{\sigma^{\circ}}$

in addition: " $n_V^{\circ}$ ", and " $n_H^{\circ}$ " represents respectively the initial moles number of  $V_2O_5$  and  $H^+$ ,

" $X$ " the moles number of  $V_2O_5$  dissolved at time  $t$ , by consumption of  $2X$  moles of

$H^+$ , and releasing  $2X$  moles of  $VO_2^+$ ;

$$r_{(5)S_i} = \frac{1}{2} \frac{d[VO_2^+]}{dt} \times \frac{1}{2} \frac{d(2X)_{S_i}}{V_{suspension} dt} \times \frac{d(X)_{S_i}}{V_{suspension} dt} \times k_{(5)} \times \left( \frac{N_{\sigma i}}{N_a} \right)^{\alpha} \times \frac{\left\{ n_H^{\circ} - 2 \times (X)_{S_i} \right\}^{\beta}}{V_{suspension}^{\beta}} \times k_{(5)} \times \frac{\left\{ 2 \times (X)_{S_i} \right\}^{\gamma}}{V_{suspension}^{\gamma}} \quad (14)$$

Moreover, the following changes are required in order to transform Eq. (14) into a resolvable form:

$$N_{\sigma i} \frac{S_i}{\sigma^{\circ}} = \frac{4\pi \times N_i}{\sigma^{\circ}} R_i^2 \quad (A)$$

Besides the mass of the  $V_2O_5$  introduced into the suspension is:  $m_{V_2O_5} = m_{R_1} + m_{R_2} + m_{R_3}$

The mass of  $V_2O_5$  particles having  $R_i$  as diameter can be expressed by the two following equations:

$m_{R_i}$  Molecular weight of  $V_2O_5 \times$  mol number of particles having  $R_i$   $M \times n_{VR_i}$

$$\text{and } m_{R_i} = \rho V_{solide R_i} = \rho \frac{4\pi R_i^3}{3}$$

Combining both equations leads to:  $M \times n_{VR_i} = \rho \frac{4\pi R_i^3}{3} \Rightarrow$

$$R_i = \left\{ \frac{3M n_{VR_i}}{4\pi \rho} \right\}^{\frac{1}{3}} \quad (B)$$

Substituting (B) into (A) gives the number of sites having, at time  $t$ ,  $R_i$  as initial diameter:

$$N_{\sigma i} = \frac{4\pi \times N_i}{\sigma^{\circ}} \left( \left\{ \frac{3M n_{VR_i}}{4\pi \rho} \right\}^{\frac{1}{3}} \right)^2 \Rightarrow N_{\sigma i} = \frac{N_i}{\sigma^{\circ}} \times \left( \frac{3(4\pi)^{0.5} M n_{VR_i}}{\rho} \right)^{2/3}$$

And substituting  $n_{VR_i}$  by  $(n_V^{\circ} - X_{R_i})$  gives  $\Rightarrow$

$$N_{\sigma i} = \frac{N_i}{\sigma^{\circ}} \times \left( \frac{3(4\pi)^{0.5} M}{\rho} \right)^{2/3} \times (n_V^{\circ} - X_{R_i})^{2/3} \quad (C)$$

Substituting (C) into the expression of the rate (Eq. (14)) leads to:

$$r_{(5)S_i} = \frac{d(X)_{S_i}}{V_{suspension} dt} \times k_{(5)} \times \left( \frac{N_i}{N_a \times \sigma^{\circ}} \times \left( \frac{3(4\pi)^{0.5} M}{\rho} \right)^{2/3} \right)^{\alpha} \times (n_V^{\circ} - X_{R_i})^{2/3} \times \frac{\left\{ n_H^{\circ} - 2(X)_{S_i} \right\}^{\beta}}{V_{suspension}^{\beta}} \times k_{(5)} \times \frac{\left\{ 2(X)_{S_i} \right\}^{\gamma}}{V_{suspension}^{\gamma}}$$

$$r_{(5)S_i} = \frac{d(X)_{S_i}}{dt} \times k_{(5)} \left( \frac{N_i}{N_a \times \sigma^{\circ}} \times \left( \frac{3(4\pi)^{0.5} M}{\rho} \right)^{2/3} \right)^{\alpha} \times (n_V^{\circ} - X_{R_i})^{2/3} \times \frac{\left\{ n_H^{\circ} - 2 \times (X)_{S_i} \right\}^{\beta}}{V_{suspension}^{\beta}} \times k_{(5)} \times \frac{\left\{ 2 \times (X)_{S_i} \right\}^{\gamma}}{V_{suspension}^{\gamma}}$$

The size of all these equations appears to be so high!! why??? To solve this equation, the reaction orders are required and they will be assumed to be equal to the stoichiometric coefficients of each reactant, i.e.  $\alpha = 1$  and  $\beta = \gamma = 2$ .

$$r_{(5)S_i} \frac{d(X)_{S_i}}{dt} = k_{(5)} \times \frac{N_i}{N_a \times \sigma^o} \times \left( \frac{3(4\pi)^{0.5} M}{\rho} \right)^{2/3} \times (n^o_v X_{R_i})^{2/3} \times \frac{\{n^o_H \quad 2 \times (X)_{S_i}\}^2}{V_{suspension}} \quad k_{(5)} \frac{\{2 \times (X)_{S_i}\}^2}{V_{suspension}} \quad (15)$$

Note that three equations must be solved for the three particle sizes chosen, each one providing the mole number of  $VO_2^+$  produced by the dissolution of the corresponding family of these particles as indicated in the following table.

	$r_{(5)S_1}$	$r_{(5)S_2}$	$r_{(5)S_3}$
Dissolution rate relative to the particles having, at time t, an average Radii $R_i$ (i going from 1 to 3, as defined above)			
the number of the particles having, at time t, an average Radii $R_i$	$N_1$	$N_2$	$N_3$
The mole number of $VO_2^+$ produced by the dissolution of the particles having, at time t, an average Radii $R_i$	$2X_{R_1}$	$2X_{R_2}$	$2X_{R_3}$
Total mole number of $VO_2^+$ produced by the dissolution of all the particles at the time t	$2X$	$2X_{R_1} + 2X_{R_2} + 2X_{R_3}$	

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