



# Evaluation of additive formulations to inhibit precipitation of positive electrolyte in vanadium battery



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## HIGHLIGHTS

- Viscosity above 3.5 M V(V) electrolyte in 5.7 M H<sub>2</sub>SO<sub>4</sub> increases exponentially.
- Inorganic additives performed better than organic ones to inhibit precipitation.
- Developed additive KS11 prevents precipitation of 4 M V(V) electrolyte up to 50 °C.
- The developed additives inhibits precipitation of V(IV) species around 5–20 °C.

## ARTICLE INFO

### Article history:

Received 21 September 2016

Received in revised form

10 November 2016

Accepted 19 November 2016

Available online 24 November 2016

### Keywords:

Vanadium battery

Positive vanadium electrolyte

Scale inhibitor

Additive

V(V) precipitation

## ABSTRACT

A comprehensive study has been performed to develop blended additive formulations based on organic and inorganic compounds to prevent the precipitation of supersaturated V(V) species in the Vanadium Flow Battery at high temperatures around 50 °C. It was found that organic formulations are oxidized by the strong oxidizing effect of V(V) species and are hence ineffective. The inorganic additive formulation KS11 which consists of 1 wt% of K<sub>3</sub>PO<sub>4</sub> 1 wt% of SHMP appears to be very effective with a vanadium solution of composition 3.5 M V(V) in total sulphate/bisulphate concentration of 5.7 M up to a temperature of 40 °C. The phosphate ions (PO<sub>4</sub><sup>3-</sup>) released from K<sub>3</sub>PO<sub>4</sub> and PO<sub>3</sub><sup>2-</sup> ions from SHMP (NaPO<sub>3</sub>)<sub>6</sub> are believed to adsorb onto the nucleating ions, thus inhibiting the precipitation of scale forming species, or adsorption onto the growing crystals, deforming and/or inhibiting further formation of vanadium crystals.

Although the electrochemical activity of 3.5 M V solutions was unaffected in the presence of the KS11, increasing vanadium concentration above 3.5 M and total sulphate/bisulphate concentration above 6 M is probably increasing the formation of electrochemically inactive complexes of vanadium-sulphate and polyvanadic species. This results in increased solution viscosity and subsequently reduces the electrochemical activity exponentially.

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## 1. Introduction

To utilize the electricity generated from intermittent renewable energy sources such as photovoltaic (PV) or wind, large scale electricity storage systems are inevitable. Therefore, demand for large scale electricity storage systems is increasing for various applications like remote area power supply systems, telecommunication installations, offshore platforms, emergency back-up

systems.

One of the mature large scale electricity storage technologies currently available is the vanadium flow battery (VFB). The VFB consists of mainly three basic components: (i) electrolytes, (ii) membranes and (iii) electrodes. The flow cell comprises positive half-cell and negative half-cell. The two half cells are separated by a membrane, which prevents cross mixing of the two different type of electrolyte (positive and negative electrolytes). An inert electrode made of highly porous carbon felt is placed in each side of the cell. The electrolytes, both positive electrolyte and negative electrolyte, are stored in two external electrolyte storage tanks. The rechargeable electrolytes are circulated through the inert porous

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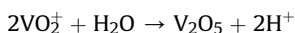
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carbon felt electrodes where the electrochemical reactions occur. The V(II)/V(III) redox couple is introduced in a negative half-cell and V(IV)/V(V) redox couple in the positive half-cell to perform a reversible reaction. A schematic of the VFB is shown in Fig. 1.

The vanadium electrolyte is the most important component of the vanadium flow battery. It is basically electricity storage medium besides, the conductor of the ions. Hence, the capacity of the battery is determined by the vanadium electrolyte concentration and subsequently the volume of the electrolyte which ultimately determines the energy density of the battery. Although the energy density of the VFB is presently on the lower side but for most stationary electricity storage applications it is adequate. However, improvement in energy density of the VFB will help to lower the volume and weight of the battery that may enhance the marketability.

The precipitation of the negative electrolytes [V(II) and V(III)] at temperatures below 10 °C and positive electrolytes [V(V)] at temperatures above 40 °C currently limits the energy density of the vanadium battery to 20–25 Wh/kg when vanadium concentrations are in the range of 1.6–2.0 M. Improved stability of the vanadium electrolyte is therefore, also desirable for a wider operating temperature range.

One of the main aims of this study was to improve the stability of supersaturated V(V) solutions at higher temperatures so as to increase the energy density of the vanadium flow battery. Rahman [1] in 1998 found that the precipitation rates in vanadium solutions with vanadium concentrations of V(V) species above 3 M were significantly fast. Thermal precipitation of supersaturated V(V) solutions occurs according to the following reaction:



Thermal precipitation of V(V) ions can thus be suppressed by increasing the concentration of sulfuric acid that increases the proton concentration, thus shifting the above equilibrium to the left. Increasing the sulfuric acid concentration will however, enhance the precipitation of V(II), V(III) and V(IV) species due to the common ion effect of the sulphate ions. In the VFB, the total sulphate concentration was therefore, set between 4 and 5 M while the maximum vanadium ion concentration was 2 M.

A comprehensive investigation was thus undertaken by Rahman [1] to stabilise supersaturated V(V) solutions of concentration above 3 M by using various antiscalant. The main focus of the study

was on increasing the induction times of vanadium solution (V(V) species) in different total concentrations of sulphate/bisulphate and at various temperatures using precipitation inhibitors.

The addition of scale control chemicals to prevent the formation of scale in a variety of applications such as cooling towers, boilers, desalination plants, oil wells etc. is well known. Presently methods of inhibiting scale formation using chemicals in the water treatment industry are known as threshold agents. The addition of less than stoichiometric amounts of specific polyphosphates or polyphosphonates to supersaturated solutions of brines has been shown to inhibit the precipitation for substantial periods of time (Rice and Partridge [2]; Buehrer and Reitemeier [3]).

The specific mechanism of minimization of scale formation by threshold activity is not fully understood but it is strongly believed that a common feature of threshold agents is sequestration or the capability of forming stable complexes with polyvalent cations thus preventing precipitation. Supersaturated solutions of brines are evidently stabilised by threshold agents in some manner involving alteration and distortion in crystal morphology at the time of nucleation and/or subsequent inhibition during growth rate (Spiegler and Laird [4]).

Logan and Walker [5] are of the opinion that additives may act to stifle formation of scale by one of the following routes: (i) additives may change the precipitating salt's chemical potential by affecting complex formation and adsorption; (ii) they may adsorb onto the precipitating ions, thus inhibiting the scale formation at nucleation step; (iii) they may adsorb onto the surface of growing crystals, thus distorting and/or preventing further crystal formation. It is possible that precipitation is minimized through more than one of the above routes. However, it is well known and fully established that once supersaturation occurs in any aqueous system, *precipitation is inevitable*, regardless of the merits of all known or available threshold agents or blended formulations.

Therefore, if the induction time for the onset of precipitation can be increased sufficiently, it would be possible to increase the energy density of vanadium flow battery by employing supersaturated vanadium solution in the presence of appropriate additives or blended formulation which inhibits precipitation. Skyllas-Kazacos and co-workers initially proposed the use of stabilizing agents for inhibiting precipitation in supersaturated vanadium solutions in 1994 (Skyllas-Kazacos [6,7]). Rahman [1] extended the work on screening various inhibitors to prevent the precipitation of concentrated V(V) electrolytes, while sodium hexa-meta-phosphate and potassium sulphate were reported to inhibit precipitation of supersaturated V(IV) electrolyte by Skyllas-Kazacos et al. [8]. Recently a number of researchers have diverted their attention towards the vanadium battery particularly on the investigation of additives to stabilise the supersaturated vanadium electrolytes.

Li et al. [9] investigated organic additives such as fructose, mannitol, glucose, d-sorbitol to inhibit the precipitation of positive electrolyte. They stated that d-sorbitol exhibits the best electrochemical performance. In terms of energy efficiency, d-sorbitol demonstrated a slightly higher average value of 81.8% compared to 79.8% for the electrolyte without additives. Wu et al. [10] employed organic additives such as inositol and phytic acid to improve the stability and electrochemical reversibility of positive vanadium electrolyte. They reported that the thermal stability of V(V) electrolyte was found to be improved by both additives. Effects of organic inhibitors containing  $\text{NH}_2$  and  $\text{SO}_3\text{H}$  on electrochemical behaviour of VFB were reported by He et al. [11]. They found that amino-methyl-sulfonic acid (AMSA) and methane-sulfonic acid (MSA) can inhibit the precipitation of V(V) solutions at higher temperatures. However, in our opinion, it appears that a significant improvement in stability could not be achieved

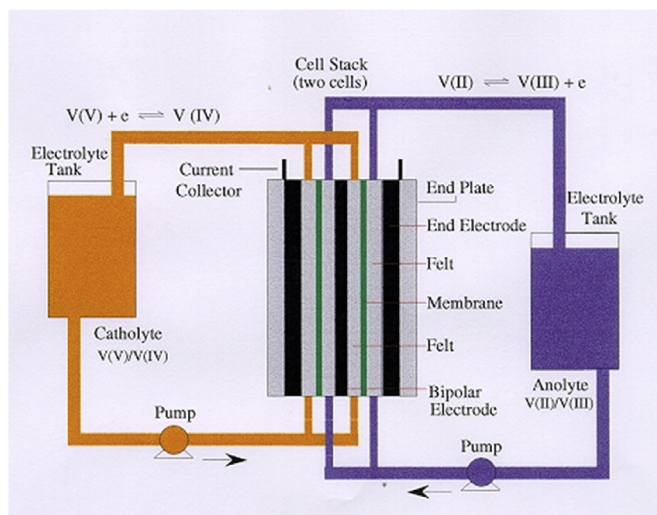


Fig. 1. Main components of vanadium flow battery [1].

by organic additives probably due to the strong oxidizing nature of V(V) ions that will interact with organic additives and affects their efficiency.

Chang et al. [12] studied the Coulter dispersants IIIA (containing coconut oil amine adducts with 15 ethylene oxide groups) as an additive for stabilizing positive electrolyte concentrations above 1.8 M vanadium ions. Wang et al. [13] investigated several compounds as additives over the temperature range of 5–60 °C to improve the stability and electrochemical activity of the V(V) electrolyte for (VFB). They found that sodium ligninsulfonate (SL), methyl orange (MO), sodium dodecyl sulphate (SDS), Triton X-100 (OP) and polyvinyl alcohol (PVA) increases the stability of V(V) electrolyte in the range of 5–45 °C. Liu et al. [14] evaluated the performance of DL-malic acid and L-aspartic acid to improve the stability and electrochemical activity of V(III) electrolyte. The stability experiments indicated that the addition of L-aspartic acid in 2 M V(III) solution can stabilise the electrolyte by retarding its precipitation.

Park et al. [15] studied the inorganic additive sodium pyrophosphate tetrabasic (SPT) to enhance the stability of positive electrolyte (2 M V(V) solution in 4 M total sulfates) with 0.05 M SPT. They reported that the addition of SPT can effectively delay the precipitation of V(V) ions in the positive electrolytes. Wang et al. [16,17] made efforts to extend the operating temperature of vanadium battery electrolyte in the range of –5 to 45 °C by utilizing methanesulfonic acid, boric acid hydrochloric acid, trifluoroacetic acid, polyacrylic acid, oxalic acid, methacrylic acid and phosphotungstic acid. The stability and electrochemical behaviour of the V(V) electrolyte with and without several organic amines with  $-NH_2$  functional groups and inorganic ammoniums with  $-NH_4^+$  functional groups were studied and compared. The effect of mechanism of  $-NH_2$  and  $NH_4^+$  groups in the preferred additives on the stability of V(V) electrolyte was proposed and discussed.

The use of ammonium phosphate, ammonium sulphate, sodium pentapolyphosphate and Orotan 1124 was shown to stabilise 2 M V(III) solutions at temperatures as low as 5 °C [18]. Cell cycling experiments confirmed that ammonium phosphate could dramatically extend cell operation of a 2 M vanadium solution without precipitation over more than 250 cycles at 5 °C, compared with less than 15 cycles for a blank solution without additives. Kauser et al. [19] presented the results of inorganic additives at 45 °C by employing 2 M vanadium electrolyte in a redox flow cell. When the blank solution was tested in a flow cell, a sudden drop in capacity was observed followed by pump failure after about 70 cycles; while the flow cell with vanadium solution containing additives continue to run without failure for about 120 cycles for ammonium sulphate and 150 cycles for ammonium phosphate.

In addition to extending the lower operating temperature range however, it is of interest to increase the upper temperature limit above 45 °C as well. Most of researchers have employed 2 M vanadium electrolyte for studying the effect of additives. In the present study a systematic evaluation of various additives was undertaken to retard the precipitation of V(V) species from supersaturated V(V) solutions in sulfuric acid at V(V) concentrations of 4 M and up to temperatures of 50 °C. The function of the threshold inhibitor would be to retard precipitation for a sufficiently long period of time so that the supersaturated V(V) ions transform to V(IV) ions during battery operation before the induction time or retardation time is exceeded. Even though the main purpose of this study was to focus on prevention of V(V) thermal precipitation, since the V(V) solutions during charge and discharge cycling undergo changes from V(V) to V(IV), it was necessary to also evaluate selected additives against precipitation of V(IV) electrolyte at low temperatures as well.

## 2. Experimental procedure

Supersaturated vanadium (V) solutions of different vanadium concentrations namely 2 M, 3 M, 4 M and 5 M prepared in different sulfuric acid concentrations containing 5 M, 6 M and 7 M total sulphate/bisulphate were prepared for studying the stability and kinetics of thermal precipitation. All of these vanadium(V) solutions were prepared by first reacting  $V_2O_3$  powder and  $V_2O_5$  powder in the desired concentration of sulfuric acid and then carrying out electrolytic oxidation of the resultant V(IV) solution. From each vanadium(V) solution, samples of about 30 ml were taken in glass bottles of capacity 40 ml with teflon stoppers and placed in constant temperature water baths maintained at 30, 40 and 50 °C. A temperature controlled immersion circulator (Thermoline) water bath capable of controlling the temperature to an accuracy of  $\pm 0.5$  °C was used to maintain the constant temperature.

Each additive was added to the V(V) solution on the weight percent (wt%) basis at various dose levels. The additive was mixed thoroughly by shaking the bottle for about 5 min. After taking the initial sample, the bottles were placed in the water bath at the desired temperature. Liquid samples were taken periodically using a 0.45  $\mu$ m Millipore filter and diluted as discussed earlier for the stability evaluation experiments. The vanadium concentration was analysed by atomic absorption spectroscopy (AAS). Although it was difficult to visually see the onset of precipitation because of the dark brownish red colour of the supersaturated V(V) solutions, the solutions were monitored daily to note the time elapsed for the initial appearance of any precipitate. The true indication of precipitation was however, determined by the decrease in concentration of the V(V) solutions measured by periodic sampling.

Since the solubility of V(IV) decreases with decreasing temperature, the evaluation of additives to prevent precipitation of supersaturated V(IV) solutions was carried out at 20 °C using a similar procedure as described above.

The initial screening of the additives to prevent thermal precipitation of supersaturated V(V) solution was carried out at 50 °C using 4.7 M V(V) solution in 6 M total sulphate/bisulphate. Without additives, this solution precipitated within a day. Because the V(V) solution in its discharged condition transforms to the V(IV) oxidation state, the additives that were found to be good inhibitors for V(V) precipitation were again tested to evaluate the effectiveness against precipitation of V(IV) solution. Formulations were then developed by blending two or more additives that showed promising results for both V(V) and V(IV) solutions to see if they could make any improvement over individual additives.

The newly developed formulations were evaluated using 4 M V(V) solution in 6 M total sulphate/bisulphate at 40 °C. The successful formulation was further studied at different dose levels to identify the optimum dosage and its performance was evaluated on a long term basis to inhibit V(V) precipitation at various temperatures, V(V) concentrations and total sulphate/bisulphate concentration. Finally some selected formulations were tested to evaluate their effectiveness in preventing the precipitation of supersaturated V(II), V(III) and V(IV) solutions. The effect of these additives on the electrochemical reversibility of the vanadium redox couple reactions was also evaluated using Cyclic Voltammetry (CV).

## 3. Results and discussion

### 3.1. Preliminary screening of additives

A large number of scale inhibitors which are generally used to prevent precipitation of carbonate and sulphate scales in desalination plants, cooling towers and oil wells at high temperatures were screened to inhibit thermal precipitation of supersaturated

V(V) solutions at 50 °C. Some promising additives tested earlier by Skyllas-Kazacos and Kazacos [6] were also included in the initial screening under identical conditions. These additives contain charged or neutral but polar functional groups mainly responsible for inhibiting the precipitating ions. It has been reported by Davey [20] and Amjad [21] that structural matching between the functional groups of the additives and the cations at the crystal surface plays an important role in assessing the effectiveness of the additives. The molecular structures of some antiscalants evaluated in this study are shown in Fig. SI-1.

The performance of the additives evaluated, along with their dose level are listed in Table 1. It can be observed that sodium hexametaphosphate (SHMP), Briquest 3010-25 K of Albright and Wilson, pHFreedom of Calgon showed good performance compared to the rest of the chemicals listed in Table 1. Both pHFreedom and Briquest 3010-25 K increased induction time from 8 h to 48 h, whereas SHMP increased the induction time to 96 h.

The Calgon antiscalant, pHFreedom, is a liquid formulation of polymeric dispersants and a patented organic inhibitor [1-hydroxyethylene 1,1-diphosphonic acid, (HEDP) based] specifically designed to prevent calcium sulphate scale in mining processes and it functions both in acidic and alkaline environments without losing effectiveness. The phosphonic acid group ( $\text{CPO}_3\text{H}_2$ ) exhibits a high degree of anionic functionality, which makes it particularly useful as a cation sequestering agent. The carbon-to-phosphorous-to-oxygen bonding arrangement in these molecules is more resistant to hydrolysis (Drew [22]) and is more stable against oxidation by V(V) than the organic additives containing  $-\text{OH}$  or  $-\text{OOH}$  groups. Briquest 3010-25 K is a potassium nitrilotri(methylenephosphonate)-*N*-oxide based additive. Flocon-100, a polyacrylate, is an antiscalant for inhibiting carbonate and sulphate scales in reverse osmosis desalination plants [23]. Ethylene diamine tetra(methylene phosphonic acid), EDTMP was reported by Gill and Varsanik [24] to show very good inhibition against calcium sulphate scaling. It is reported that the anionic functional groups such as  $-\text{COOH}$  present in polyacrylic acid, polymaleic acid and

polycarboxylic acid ionise in aqueous system to release negatively charged species [22]. The electrostatic attraction between these negatively charged functional groups and positively charged V(V) ions was believed to influence the precipitation behaviour. All organic compounds showed poor performance in the V(V) solution due to the oxidizing effect of V(V) ions.

In order to see if polymeric antiscalant without charged group would have any effect on the rate of V(V) precipitation, an experiment was conducted using polyacrylamide ( $-\text{CONH}_2$ ), but again this additive also failed to prevent V(V) precipitation.

However, SHMP (a stable six-membered ring structure) was found to demonstrate better performance over long chain molecules of organic compounds. Sodium hexametaphosphate is most commonly used in reverse osmosis systems because of its low cost and good performance in waters of high calcium sulphate content. According to Reddy and Nancollas [26], SHMP provided maximum gypsum scale inhibition compared with seven other commercial organic additives they evaluated.

Since V(V) species transforms to the V(IV) oxidation state during the discharge cycle of the battery and precipitates as  $\text{VOSO}_4$  at lower temperatures, it was decided to evaluate these additives (effective in preventing sulphate scales) against V(IV) solution precipitation before conducting any further screening for V(V) solutions. Skyllas-Kazacos and Peng [8] in a separate study indicated that potassium sulphate ( $\text{K}_2\text{SO}_4$ ) showed better performance in preventing supersaturated V(IV) solution precipitation. But the performance of  $\text{K}_2\text{SO}_4$  was found to be very poor for inhibiting V(V) precipitation, which is one of the main objectives of this study. To develop a comprehensive additive, which can stabilise both V(V) and V(IV) species in the positive half-cell of the battery  $\text{K}_3\text{PO}_4$  and  $\text{KHSO}_4$  were selected as possible compounds to study the effect on their precipitation. Absence of sulphate ions in  $\text{K}_3\text{PO}_4$  was expected to give better performance for V(IV) inhibition and presence of phosphate was found to provide inhibition for V(V) solution. Table 2 shows the performance of selected chemicals against the precipitation of 4 M V(IV) solution in 6 M total sulphate/bisulphate

**Table 1**  
List of additives studied for preventing V(V) precipitation in 4.7 M V(V) solution in 6.0 M  $\text{H}_2\text{SO}_4$  at 50 °C.

Expt#	Name	Dosage (wt/vol)%	Initial appearance of precipitation (days)	Degree of precipitation <sup>a</sup> (%)
AD-0	Blank	0.0	<8 h	100
AD-1	Ammonium Carbonate	0.5	<1	100
AD-2	Polyacrylic acid	0.5	<1	50
AD-3	Polyacrylamide	0.5	<2	30
AD-24	Polymaleic acid	0.5	<2	30
AD-4	Alanine	0.5	<1	100
AD-5	Glycine	0.5	<1	100
AD-6	SodiumPolyPhos.	1.0	<1	60
AD-7	Sod.TriPolyPhos	1.0	<1	60
AD-14	Ammonium Sulphate	2.0	<1	80
AD-15	Potassium Sulphate	2.0	<1	60
AD-19	Poly Styrene S. Acid	2.0	<1	50
AD-20	Teric PE61, ICI	2.0	<1	70
AD-21	Teric BL8, ICI	2.0	<1	60
AD-9	Flocon-100	2.0	1	20
AD-17	Calgon EL-5600	2.0	2	40
AD-13	Briquest 3010-25 K	2.0	2	20
AD-18	pHFreedom	2.0	2	10
AD-8	SHMP	1.0	2	30
AD-16	SHMP	2.0	4	10

$$\% \text{ Inhibition} = \frac{[\text{V(V)}]_{\text{sample}} - [\text{V(V)}]_{\text{blank}}}{[\text{V(V)}]_{\text{initial}} - [\text{V(V)}]_{\text{blank}}} \times 100\%$$

Where:

% Inhibition = scale inhibition (%).

$[\text{V(V)}]_{\text{sample}}$  = V(V) concentration in the presence of inhibitor at t h.

$[\text{V(V)}]_{\text{blank}}$  = V(V) concentration in the absence of inhibitor at t h.

$[\text{V(V)}]_{\text{initial}}$  = V(V) concentration at the beginning of experiment t = 0.

<sup>a</sup> Degree of precipitation (%) = 100 – % Inhibition [25].



**Table 2**Effectiveness of additives studied for preventing precipitation of 4 M V(IV) solution in 6.0 M H<sub>2</sub>SO<sub>4</sub> at 20 °C [1].

Expt#	Name	Dosage (wt/vol)%	Initial appearance of precipitation (days)	Degree of precipitation (%)
AD4-0	Blank	0.0	2	30
AD4-1	K <sub>2</sub> SO <sub>4</sub>	1.0	60	few crystals
AD4-2	K <sub>3</sub> PO <sub>4</sub>	1.0	68	few crystals
AD4-3	KHSO <sub>4</sub>	1.0	2	10
AD4-4	pHreedom	1.0	6	20
AD4-5	Flocon-100	1.0	5	10
AD4-6	Calgon EL-5600	1.0	6	10
AD4-7	Briquest 3010-25 K	1.0	2	20
AD4-8	EDTMP	1.0	3	30
AD4-9	SHMP	1.0	34	10
AD4-10	CL-4000	1.0	6	10

EDTMP = Ethylene diamine tetramethylene phosphonic acid.

CL-4000 = Antiscalant by Calgon.

at 20 °C.

Surprisingly the performance of K<sub>3</sub>PO<sub>4</sub> was found to be the best among all the additives tested against precipitation of V(IV) solution and increased the induction time by 34 times relative to the Blank solution. The performance of K<sub>2</sub>SO<sub>4</sub> was also about the same as that of K<sub>3</sub>PO<sub>4</sub>, and SHMP increased the induction time of V(IV) solution by about 16 times. It was thus concluded that K<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub> and SHMP appear to prevent precipitation of supersaturated V(IV) solution significantly. These three compounds were finally evaluated in 4 M V(V) solution in 6 M total sulphate at 50 °C to see their effectiveness against thermal precipitation of supersaturated V(V) and the results are presented in Table 3.

It is obvious from Table 3 that K<sub>2</sub>SO<sub>4</sub> failed to inhibit the precipitation of V(V) solution at 50 °C whereas tri-potassium phosphate and SHMP showed better performance at a dose level of 1 mol % and increased the induction period by about 10 times. The additive EDTMP showed good performance against V(V) precipitation (see Table 3) but showed poor performance against V(IV) precipitation (see Table 2). The performance of SHMP is slightly better than K<sub>3</sub>PO<sub>4</sub> for V(V) solution but the problem with SHMP is that it is not easily soluble in vanadium solution while K<sub>3</sub>PO<sub>4</sub> dissolves quickly. In the case of V(IV) solution on the other hand, the performance of SHMP was found to be relatively inferior to K<sub>3</sub>PO<sub>4</sub>.

The additives, SHMP and K<sub>3</sub>PO<sub>4</sub> were thus found to stabilise both supersaturated V(V) and V(IV) solutions reasonably well. Therefore, further investigations were carried out by mixing these together in different proportions to develop a suitable blend for the stabilisation of both V(IV) and V(V) supersaturated solutions. Different formulations were developed by combining these two additives in various ratios and also with very small amounts of a dispersant like polystyrene sulfonic acid (PSA). The details of the formulations and their effectiveness are discussed in the following section.

### 3.2. Development of additive formulations

After evaluating these additives individually, several formulations were developed by mixing SHMP, K<sub>3</sub>PO<sub>4</sub> and PSA to establish

whether they can make any improvement. The composition of various blended formulations prepared in this study to inhibit V(V)/V(IV) precipitation are given in Table 4. In the blended formulations SP-S, KP-S and KSP-S the dispersant polystyrene sulfonic acid (PSA) was added by preparing a 10 wt% solution whereas, SHMP and K<sub>3</sub>PO<sub>4</sub> were added as solid material to the vanadium solution.

During the additive evaluation experiment it was observed that SHMP cannot dissolve easily in vanadium solution and that although K<sub>3</sub>PO<sub>4</sub> dissolves fully in vanadium solution, it sometimes sticks to the walls of the container and poses precipitation problems. So, after conducting some initial experiments, it was decided to prepare 50 wt% solution of SHMP and K<sub>3</sub>PO<sub>4</sub> separately in 1 M H<sub>2</sub>SO<sub>4</sub> and the additives were added to vanadium solution in the desired amount using these 50 wt% SHMP and 50 wt% K<sub>3</sub>PO<sub>4</sub> solutions. Distilled water was not used to prepare the additive solutions as addition of small amounts of distilled water to V(V) solution has been found to change the structure and speciation of the V(V) ions [1]. These additive solutions were prepared carefully by first taking 1 M H<sub>2</sub>SO<sub>4</sub> in the beaker and while stirring the sulfuric acid solution, SHMP or K<sub>3</sub>PO<sub>4</sub> was added in small portions until the desired amount of SHMP was dissolved fully. To add 1 wt% SHMP, 0.2 gm of 50 wt% SHMP solution was added to 10 gm of V(V)

**Table 4**

List of various formulations prepared for the prevention of V(IV)/V(V) precipitation.

Formulation ID	SHMP	K <sub>3</sub> PO <sub>4</sub>	PSA	EDTMP	1 M H <sub>2</sub> SO <sub>4</sub>
SP-S	X	—	X	—	—
KP-S	—	X	X	—	—
KSP-S	X	X	X	—	—
SP-L	X	—	X	—	X
KP-L	—	X	X	—	X
KSP-L	X	X	X	—	X
KS-L	X	X	—	—	X

SHMP: sodium hexametaphosphate; PSA: dispersant, polystyrene sulfonic acid.

EDTMP: ethylene diamine tetramethylene phosphonic acid; DW: distilled water.

1. In formulation SP-S, KP-S, KSP-S the additive SHMP and K<sub>3</sub>PO<sub>4</sub> was added as solid and PSA was added as 10% liquid in distilled water.2. In formulation SP-L, KP-L, KSP-L, KS-L the additives both SHMP and K<sub>3</sub>PO<sub>4</sub> were added by preparing 50 wt% solution in 1 M H<sub>2</sub>SO<sub>4</sub>.**Table 3**Performance of various additives studied for preventing precipitation of 4.0 M V(V) solution in 6.0 M H<sub>2</sub>SO<sub>4</sub> at 50 °C [1].

Formulation name	Dosage	Initial appearance of precipitation (days)	Degree of precipitation (%)
Blank	0.0	1	10
K <sub>2</sub> SO <sub>4</sub>	1.0 mol %	1	15
EDTMP	1.0 mol %	8	5
K <sub>3</sub> PO <sub>4</sub>	1.0 mol %	9	5
SHMP	1.0 mol %	12	5

solution. To quickly dissolve the SHMP, the temperature should not be increased. Because at high temperature metaphosphate reversion to orthophosphate occurs which reduces the effectiveness of the additive as indicated by Ostroff [27]. Details of the performance of these formulations and dosages of each additive (SHMP,  $K_3PO_4$ ) used are given in the next sub-section.

### 3.3. Evaluation of different additive formulations

The effectiveness of the formulations developed was investigated using 4 M V(V) solution in 6 M total sulphate/bisulphate at 50 °C and 4 M V(IV) solution in 6 M total sulphate/bisulphate at 20 °C. The details of their performance and dosage levels used are given in Tables 5 and 6 respectively.

The blank V(V) solution precipitated within one day at 50 °C and similarly blank V(IV) solution also precipitated within one day at 20 °C. From the analysis of the results in Tables 5 and 6 it can be stated that addition of the dispersant PSA improves the stability of V(V) solution. In the case of the precipitation of V(IV) solution however, the addition of PSA decreases the induction time from 68 days in the presence of  $K_3PO_4$  (Table 2) to 31 days for the combination of  $K_3PO_4$  + PSA. For both V(V) and V(IV) solutions however, the additives provide a dramatic increase in induction time compared with the blanks.

Systematic additive trials were conducted according to the experimental procedure described before by measuring the change in concentration of vanadium with time. Liquid formulations of SHMP (50 wt% solution) and  $K_3PO_4$  (50 wt% solution) prepared in 1 M sulfuric acid solution were used instead of adding solid additive to the V(V) solution. Fig. 2a shows the concentration profiles of V(V) solution without additive and with 2 wt% SHMP, formulation SP-L, 2 wt%  $K_3PO_4$  and formulation KP-L at 40 °C.

The addition of SHMP increased the induction time from 3 days for blank V(V) solution to about 30 days whereas the formulation SP-L demonstrated the best performance by increasing the induction time to 40 days, thus indicating that a small amount of the dispersant PSA improves the stability of the V(V) solution compared with SHMP alone.

The performance of  $K_3PO_4$  and KP-L was found to be inferior to SHMP against V(V) precipitation, but it is more effective in inhibiting the precipitation of V(IV) solutions. It was also observed that the efficiency of  $K_3PO_4$  in retarding the precipitation of V(V) solution is reduced by addition of PSA. The relative performance of the additives in inhibiting V(V) precipitation can thus be rated as SP-L > SHMP >  $K_3PO_4$  > KP-L.

Since  $K_3PO_4$  is more effective for V(IV) solution and SHMP is better for controlling V(V) precipitation, mixtures of these two

additives were tested at 40 °C with and without dispersant and EDTMP. The effectiveness of these formulations is illustrated in Fig. 2b.

The performance of KS (2 wt% SHMP + 2 wt%  $K_3PO_4$ ) and SP-L (2 wt% SHMP + 0.02% PSA) was found to be equally good without any drop in V(V) concentration for 1000 h and with an increase in the induction time from 3 days to 40 days. The second formulation in the order of merit was KSPE (2 wt% SHMP + 2 wt%  $K_3PO_4$  + 0.5% EDTMP + 0.02% PSA) which increased the induction time of V(V) solution to 16 days with a V(V) concentration of 3.6 M after 1000 h. The formulation KSP (2 wt% SHMP + 2 wt%  $K_3PO_4$  + 0.02% PSA) extended the induction time to about 15 days but the final V(V) concentration dropped to 3.1 M after 1000 h. Although KS and SP-L were found to be equally good, the presence of  $K_3PO_4$  in the formulation KS was found to enhance the inhibition of V(IV) precipitation and has definite benefit over SP-L. Therefore, formulation KS (SHMP +  $K_3PO_4$ ) was considered as the best among all the formulations developed in this study to prevent precipitation of supersaturated V(IV) and V(V) solutions.

The influence of additives on  $V_2O_5$  precipitation reaction rates can be explained in this study in terms of the following two effects, (i) direct chelation with the crystal lattice ions in the solution, and (ii) adsorption of the additive onto the precipitating ion, thus inhibiting scale nucleation, or adsorption onto the growing crystals, thus distorting and/or inhibiting further crystal formation.

The phosphates [SHMP ( $NaPO_3$ )<sub>6</sub> and  $K_3PO_4$ ], present in the formulation KS for the control of  $VO_2^+$  ions precipitation may be forming stable chelate complexes like  $(VO_2)_3PO_4$  as reported by Silva and Ogasawara [28]. To prevent precipitation, it is not necessary to complex all the scale forming cations ( $VO_2^+$ ), but only enough to reduce the concentration so that the solubility limit is not exceeded [27].

Another possible mechanism for the inhibition of V(V) precipitation may be due to the adsorption of inhibitors on the crystal surface. Inorganic phosphates such as polyphosphates work on the principle of the threshold-effect treatment. Sub-stoichiometric levels of the phosphates are normally required and as the crystals begin to grow, the phosphate ions adsorb onto the nuclei of these developing crystals and inhibit further growth. Thus, it is possible for a small amount of phosphate to tie up a large amount of scale-forming material. The most active threshold agent in this group is SHMP (Liu and Nancollas, [29]; Gevecker, [30]; Spiegler and Laird, [4]). Since the formulation KS contains a smaller concentration of phosphate than that of the  $VO_2^+$  ion, an adsorption process appears to offer a more feasible explanation.

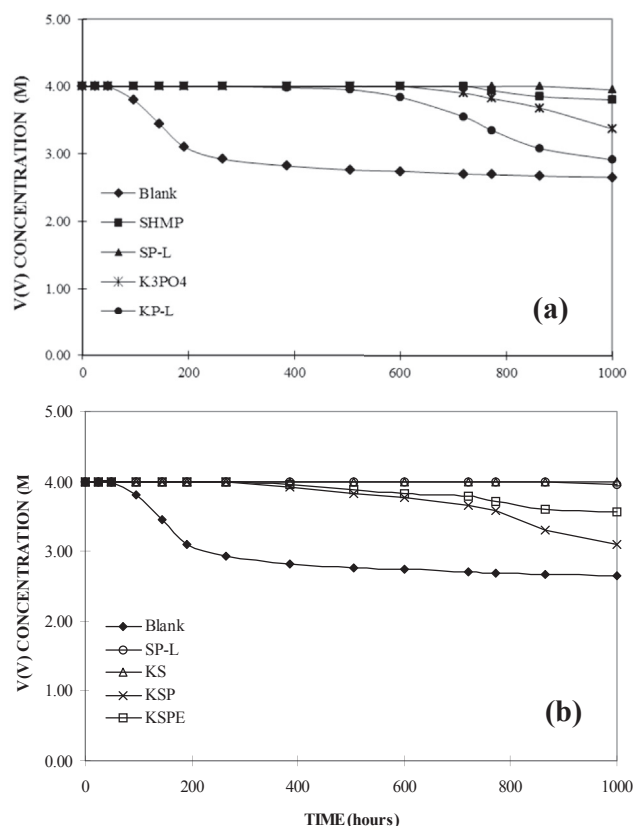
It is however likely that the formulation KS functions through both of the above mentioned routes. The phosphate ions ( $PO_4^{3-}$ )

**Table 5**  
Performance of Various formulations studied for inhibiting precipitation of 4.0 M V(V) solution in 6.0 M  $H_2SO_4$  at 50 °C.

Formulation	Dosage	Initial appearance of precipitation (days)	Degree of precipitation (%)
Blank		0.0	10
SP-S	2.3 wt% SHMP + 0.1 wt% PSA	16	slight ppt
KP-S	2.0 wt% $K_3PO_4$ + 0.1 wt% PSA	12	slight ppt
KSP-S	1.3 wt% $K_3PO_4$ + 0.7 wt% SHMP + 0.1 wt% PSA	16	slight ppt

**Table 6**  
Effectiveness of various formulations to inhibit precipitation of 4 M V(IV) solution in 6.0 M  $H_2SO_4$  at 20 °C.

Formulation	Dosage	Initial appearance of precipitation (days)	Degree of precipitation (%)
Blank	0.0	1	few crystals
SP-S	2.3 wt% SHMP + 0.1 wt% PSA	21	few crystals
KP-S	2.0 wt% $K_3PO_4$ + 0.1 wt% PSA	31	few crystals
KSP-S	1.3 wt% $K_3PO_4$ + 0.7 wt% SHMP + 0.1 wt% PSA	29	few crystals



**Fig. 2.** Precipitation behaviour of 4 M V(V) solution in 6 M total sulphate/bisulphate with different inhibitor formulations at 40 °C [1]. In Fig. 2a → SHMP = 2 wt%; SP-L = 2 wt% SHMP + 0.02% PSA; K<sub>3</sub>PO<sub>4</sub> = 2 wt%; KP-L = 2 wt% K<sub>3</sub>PO<sub>4</sub> + 0.02% PSA. In Fig. 2b → SP-L = 2 wt% SHMP + 0.02% PSA; KS = 2 wt% SHMP + 2 wt% K<sub>3</sub>PO<sub>4</sub>. KSP = 2 wt% SHMP + 2 wt% K<sub>3</sub>PO<sub>4</sub> + 0.02% PSA. KSPE = 2 wt% SHMP + 2 wt% K<sub>3</sub>PO<sub>4</sub> + 0.5% EDTMP + 0.02% PSA.

released from K<sub>3</sub>PO<sub>4</sub> may be forming a stable complex with the VO<sub>2</sub><sup>+</sup> ions such as (VO<sub>2</sub>)<sub>3</sub>PO<sub>4</sub> and PO<sub>3</sub> from SHMP (NaPO<sub>3</sub>)<sub>6</sub> block crystal growth by surface adsorption onto the active sites. While the above mechanisms could be used to explain the observed experimental trends with different additives, it is interesting to note that it is still difficult to predict how a particular compound might behave as a precipitation inhibitor, and as pointed out by Gill and Varsanik [24] and Myerson [31], scale inhibitors are still actually tested individually on a trial and error basis for their application.

Other formulations KSP and KSPE developed in this study did not perform very well. The formulation KSP was developed by adding a minute amount of PSA in order to keep any precipitation if initiated, in the dispersed form and prevent or delay further growth (Porteous, [32]). But the experimental data revealed that the performance of KSP against precipitation of V(V) solutions deteriorated with the addition of dispersant, probably because of interaction of V(IV) ions (present in small quantities in V(V) solution, about 3–4%) with PSA.

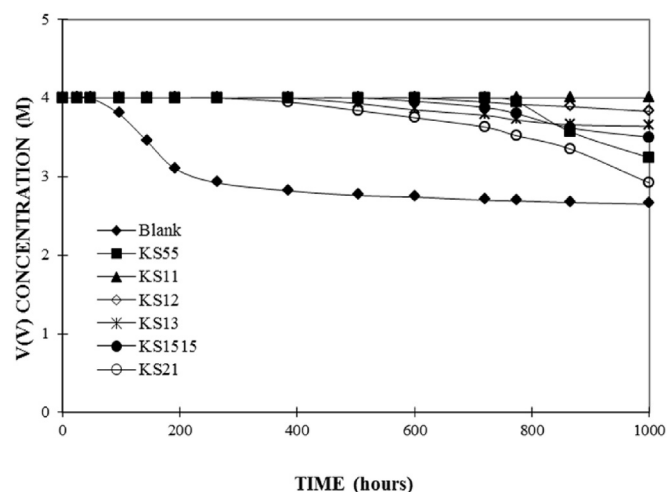
It is well known that organic phosphates exhibit a high degree of anionic functionality and stability which makes them particularly useful for sequestering cations in the desalination industry [22]. It was thought that addition of a small amount of EDTMP to KS might improve the performance against V(V) precipitation, however the performance did not improve. The reason for poor performance may be the oxidation of EDTMP by V(V) ions thus reducing its ability to inhibit precipitation. Similar oxidation of organic compounds like hydroxycarboxylic acids, D-galacturonic acid and carbohydrates by V(V) ions has been reported by Micera et al. [33].

The formulation KS was further evaluated at different dose levels of SHMP and K<sub>3</sub>PO<sub>4</sub> to optimise the amounts of each additive. The effectiveness of formulation KS was later investigated against the precipitation of V(IV) species, which is the discharged state of the vanadium ions in the positive half-cell. The formulation KS was also evaluated against precipitation of V(II) and V(III) electrolyte in the negative half-cell of the vanadium redox battery with a view to find whether it can act as a comprehensive additive for both the positive as well as the negative half-cell of the battery. If the formulation KS can inhibit the precipitation of all the four species of vanadium, it will be convenient to mix the additives in the beginning to a vanadium solution of 50% V(III) + 50% V(IV) (i.e. V<sup>3.5+</sup>) and start the battery.

### 3.4. Dosage optimization of formulation KS

The formulation KS was studied by mixing SHMP and K<sub>3</sub>PO<sub>4</sub> in different ratios to achieve the maximum induction time for the V(V) solutions. The details of various blends of formulation KS investigated using 4 M V(V) solution in 6 M total sulphate/bisulphate are given in Tables SI–1 and the performance of these blends is illustrated in Fig. 3. It can be observed from Fig. 3 that increasing the concentration of SHMP and K<sub>3</sub>PO<sub>4</sub> improved the performance of additive blend KS till it reaches 1 wt% K<sub>3</sub>PO<sub>4</sub> and 1 wt% SHMP (blend KS11). Further increase in the amount of SHMP and K<sub>3</sub>PO<sub>4</sub> (blends KS12, KS13, etc) however, dropped the performance. At low additive concentrations, inhibition of V(V) precipitation occurs through additive adsorption onto the nucleating crystals. However, at higher additive levels, the precipitation process may just be stimulated when the additive acts as a template for nucleation.

Such a behaviour has been observed in practical situations where the cations of the sparingly soluble salts in the solution can sometimes form insoluble tiny particles with the inhibitor molecules above a certain dosage level. This additive dosage level is not fixed, but is largely dependent on the type of the salt, the type of additives, the presence of other ingredients such as complexing agents in the solution and their respective concentrations [Van der Leeden and Van Rosmalen, [34]]. Logan and Kimura [35] while discussing the control of calcium sulphate scale on reverse osmosis membranes indicated that lower SHMP dosage resulted in better control than the higher dosage. Amjad et al. [36] reported that in



**Fig. 3.** Effect of different blends of formulation KS on precipitation of V(V) solution at 40 °C. KS55 = 0.5 wt% K<sub>3</sub>PO<sub>4</sub> + 0.5 wt% SHMP; KS11 = 1 wt% K<sub>3</sub>PO<sub>4</sub> + 1 wt% SHMP. KS12 = 1 wt% K<sub>3</sub>PO<sub>4</sub> + 2 wt% SHMP; KS13 = 1 wt% K<sub>3</sub>PO<sub>4</sub> + 3 wt% SHMP. KS21 = 2 wt% K<sub>3</sub>PO<sub>4</sub> + 1 wt% SHMP; KS1515 = 1.5 wt% K<sub>3</sub>PO<sub>4</sub> + 1.5 wt% SHMP.

desalination plants polyphosphates are considered as good anti-scalants, but suffer from the disadvantage of being susceptible to hydrolysis under certain conditions. The resultant phosphate ion can then react with calcium to form calcium phosphate.

From Fig. 4, it can be suggested that the blend KS11 which consists of 1 wt%  $K_3PO_4$  and 1 wt% SHMP showed the best performance over all other combinations with only a 2% decrease in V(V) concentration after 40 days. The blends KS55 and KS12 also demonstrated better performance, while KS13, KS1515 and KS21 dropped induction time significantly.

Therefore, formulation KS11 was considered as optimum and it was finally selected for the long term evaluation against V(V) thermal precipitation at 40 °C and to study the effect of various parameters like initial V(V) concentration, temperature and total sulphate/bisulphate concentration.

### 3.5. Performance evaluation of KS11

#### 3.5.1. Long term performance evaluation of KS11

The effectiveness of the formulation KS11 was further evaluated on a long term basis for about 2400 h using 4 M V(V) solution in 6 M total sulphate/bisulphate. The 4 M V(V) solution prepared earlier for the precipitation study was used for the evaluation of KS11. The blank solution started precipitating after 3 days and reached an equilibrium concentration of about 2.5 M, whereas addition of KS11 to the V(V) solution increased the induction time to about 40 days with final V(V) concentration of 3.2 M after about 100 days. The stability of 4 M V(V) solution in 6 M total sulphate/bisulphate was thus increased by about 13 times with the additive KS11 and the final V(V) concentration dropped by about 20% compared to 38% for blank V(V) solution. If the V(V) solution in the vanadium redox battery is discharged within a period of one month therefore, the formulation KS11 may be used safely to prevent the precipitation of 4 M V(V) solution in 6 M total sulphate/bisulphate. Although the precipitation with additive KS11 will begin after 40 days, the concentration of V(V) will reach 3.2 M after 60 days thus indicating an increase in the stability of V(V) species.

It was observed that a small addition of formulation KS11 has markedly decreased the precipitation rate. The inhibition can be attributed to the combination of both stable complex formation of phosphate ions with  $VO_2^+$  ions and adsorption of additive on the crystal surface.

The analysis of the liquid samples using ICP was carried out to

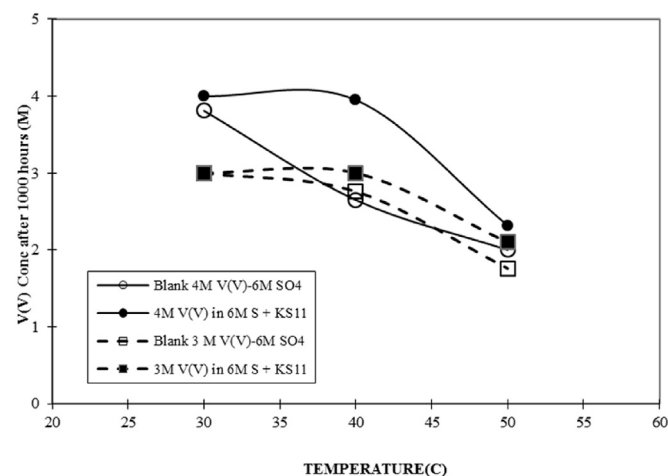


Fig. 4. Effect of temperature on performance of formulation KS11 using 3 M V(V) and 4 M V(V) solution in 6 M total sulphate/bisulphate after 1000 h. KS11 = 1 wt%  $K_3PO_4$  + 1 wt% SHMP.

detect the amounts of additives present in the solution at the start of the additive experiment and after 1000 h. About 60% active additive (P and K) was still found in the solution after 1000 h. The loss of a large amount of the original additive in the solution indicates that it has probably adsorbed onto the crystal surface or complexed with  $VO_2^+$  ions [Reddy and Nancollas, [26]].

On the basis of long term evaluation it can be concluded that the addition of additive KS11 to 4 M V(V) solution in 6 M total sulphate/bisulphate at 40 °C increases the induction time by about 13 times and decreases the precipitation rates significantly.

#### 3.5.2. Effect of temperature

The improvement in the stability of 4 M V(V) solution in 6 M total sulphate/bisulphate with KS11 was studied at different temperatures of 30, 40 and 50 °C. The final V(V) concentrations after 1000 h at these temperatures are plotted in Fig. 4. The effectiveness of KS11 at 30 °C and 40 °C was very good and V(V) concentration was almost constant for 1000 h. Increasing the temperature further to 50 °C decreased the V(V) concentration from 4 M to about 2.32 M after 1000 h, a drop of about 42%.

In case of 3 M V(V) solution in 6 M total sulphate/bisulphate, the additive KS11 was able to maintain the V(V) solution concentration constant at 3 M till 40 °C and at 50 °C the V(V) concentration after 1000 h decreased to 2.10 M, a drop of 30%.

#### 3.5.3. Effect of total sulphate/bisulphate concentration

It was found earlier during stability evaluation of concentrated V(V) solutions that increasing the total sulphate/bisulphate concentration increases the stability of V(V) solutions. The effect of KS11 when added to different V(V) solutions was studied in total sulphate/bisulphate concentrations of 5 M and 6 M. The induction times measured for blank solutions and with additive KS11 in total sulphate/bisulphate concentrations 5 M and 6 M are listed in Table 7.

The effect of increasing sulfuric acid concentration for a given V(V) solution with KS11 increases induction time significantly. The

Table 7

Summary of induction times and final V(V) concentration of V(V) solutions without additive and with additive KS11 in various total sulphate/bisulphate concentrations at different temperatures.

Temperature	V(V) solutions in 5 M total sulfur			V(V) solutions in 6 M total sulfur		
	3V5S	4V5S	5V5S	3V6S	4V6S	5V6S
<b>30 °C</b>						
Induction Time (days)						
Blank V(V) soln.	8	6	2	42	28	1.5
V(V) soln. + KS11	>42	42	—	>42	>42	—
Conc after 1000 h(M)						
Blank V(V) soln.	2.46	3.33	3.5	3	3.81	4.05
V(V) soln. + KS11	3	3.91	—	3	4	—
<b>40 °C</b>						
Induction Time (days)						
Blank V(V) soln.	1	1	<1	8	3	<1
V(V) soln. + KS11	10	7	1	>42	40	8
Conc after 1000 h(M)						
Blank V(V) soln.	1.62	2.13	2.45	2.76	2.65	3.3
V(V) soln. + KS11	1.98	2.79	3.41 <sup>a</sup>	3	3.95	3.72
<b>50 °C</b>						
Induction Time (days)						
Blank V(V) soln.	<1	<1	<1	1	<1	<1
V(V) soln. + KS11	2	1	—	9	4	—
Conc after 1000 h(M)						
Blank V(V) soln.	1.24	1.56	0.49	1.76	2	2.5
V(V) soln. + KS11	1.78	2.15 <sup>a</sup>	—	2.1	2.32	—

‘—’ indicates that no experiments were conducted at those conditions.

<sup>a</sup> V(V) concentration after 500 h.



induction time of 3 M and 4 M V(V) solution in 5 M total sulphate/bisulphate was found to be 10 days and 7 days respectively whereas 3 M and 4 M V(V) solution in 6 M total sulphate/bisulphate exhibited induction times of >42 days and 40 days respectively, an improvement of about five times. This increased stability is probably due to the formation of sulphate complexes with  $\text{VO}_2^+$  ions and dimerisation of  $\text{VO}_2^+$  ions to  $\text{V}_2\text{O}_4^{2+}$  or  $\text{V}_2\text{O}_3^{4+}$  at higher sulfuric acid concentrations.

Apart from increasing the induction time, addition of KS11 and increasing sulfuric acid concentration increases the apparent equilibrium concentration. For example, the apparent equilibrium concentration of the initially 4 M V(V) solution in 5 M total sulphate/bisulphate at 40 °C was increased from 2.13 M to 2.79 M with addition of additive KS11, an improvement of 36%. By increasing total sulphate/bisulphate concentration to 6 M, the apparent equilibrium concentration of 4 M V(V) solution was raised from 2.65 to 3.95, an increase of about 50%. In addition to the dimerisation and sulphate/bisulphate complex formation, the excess  $\text{H}^+$  ions available at higher sulfuric acid concentrations are responsible for shifting the  $\text{V}_2\text{O}_5$  precipitation equilibrium towards the formation of  $\text{VO}_2^+$  ions thus increasing the apparent equilibrium V(V) concentration.

Therefore, it can be recommended that a 4 M V(V) solution in 6 M total sulphate/bisulphate with addition of KS11 (1 wt%  $\text{K}_3\text{PO}_4$  + 1 wt% SHMP) can be used in the vanadium redox battery up to a temperature of 40 °C without precipitation for about 40 days.

However, a slightly lower total sulphate concentration will enhance the stability of the V(IV) species, which exists in the discharged state in the positive half-cell of the battery. Therefore, the stability of a 3.5 M V(V) solution in 5.7 M total sulphate/bisulphate was investigated with and without additive KS11 at 40 °C. An induction time of 25 days was observed with the blank solution and addition of KS11 increased the induction time to about 60 days. The addition of KS11 also increased the apparent equilibrium concentration of V(V) solution to 3.21 M as compared to blank V(V) solution equilibrium concentration of 2.72 M. Decreasing V(V) concentration to 3.5 M allowed a slight decrease in total sulphate/bisulphate concentration to 5.7 M with a reasonable induction time of 25 days. Addition of KS11 makes this composition (3.5V–5.7 S) more attractive with an induction time of about 60 days and an apparent equilibrium V(V) concentration of 3.21 M.

The electrochemical behaviour of the supersaturated V(V) solutions was also investigated using cyclic voltammetry. A typical CV scan obtained for V(V) solution of concentration 4 M in 5, 6 and 7 M

total sulphates using a glassy carbon electrode at a scan rate of 0.02 V/s is shown in Fig. 5. It can be observed from Fig. 5 that the magnitude of peak current decreases as concentration of total sulphate/bisulphate increases.

It is believed that, the formation of electrochemically inactive vanadium-sulphate complexes and polyvanadic species increases with increasing the total sulphate/bisulphate concentration that subsequently increases the viscosity of the supersaturated vanadium solution. Fig. 6 illustrates the exponential increase in viscosity of vanadium solutions above 3.5 M vanadium and 6 M total sulphate/bisulphate resulting in reduction of the mobility of vanadium ionic species. The effect of formation of electrochemically inactive species and subsequent increase in viscosity results in decreasing the peak current heights of the vanadium V(V) solutions.

From the analysis of the effect of both V(V) concentration and total sulphate/bisulphate concentration, it can be concluded that the most suitable concentration of vanadium electrolyte may be 3.5 M vanadium concentration in sulfuric acid solutions having total sulphate/bisulfate concentration of 5.7 M that can provide maximum electrochemical activity in the vanadium flow battery.

### 3.6. Effect of additive addition on electrochemical behaviour

The stability of supersaturated V(V) solution can be improved by adding formulated additives to prevent thermal precipitation at higher temperatures of about 40–50 °C. The effect of the addition of the additive on the electrochemical activity of concentrated V(V) solutions was evaluated by cyclic voltammetry.

The formulation KS11 developed in this study, which showed good performance in inhibiting precipitation of V(V) solution was added to 4 M V(V) solution containing 5 M total sulphate/bisulphate. The additive dosage was about 1 wt/wt% and hand shaking of the solution was done periodically over approximately 100 h. The cyclic voltammograms obtained before KS11 addition to this V(V) solution (solid line) and after addition (broken line), at a scan rate of 0.02 V/s at a glassy carbon electrode are shown in Fig. 7. It can be observed that the two voltammograms with and without additive are very similar, and the additive addition did not affect the electrochemical behaviour of the V(V) solution.

### 3.7. Evaluation of the stability of V(II), V(III) and V(IV) solutions using KS11

The V(V) species in the positive half-cell is transformed to V(IV)

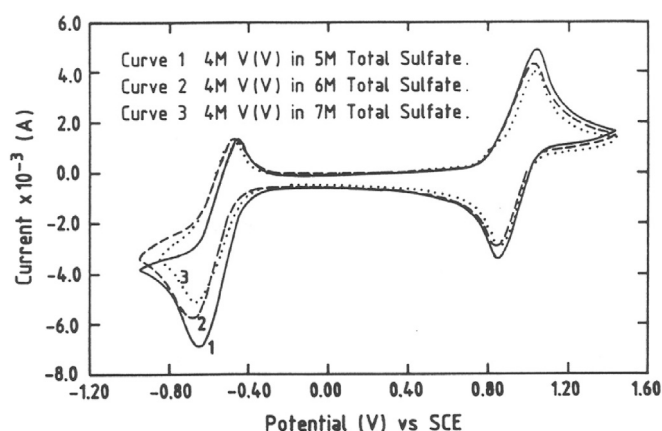


Fig. 5. Cyclic voltammogram of 4 M V(V) solution in 5, 6 and 7 M total sulphate/bisulphate at a scan rate of 0.02 V/s using glassy carbon electrode against SCE at 20 °C.

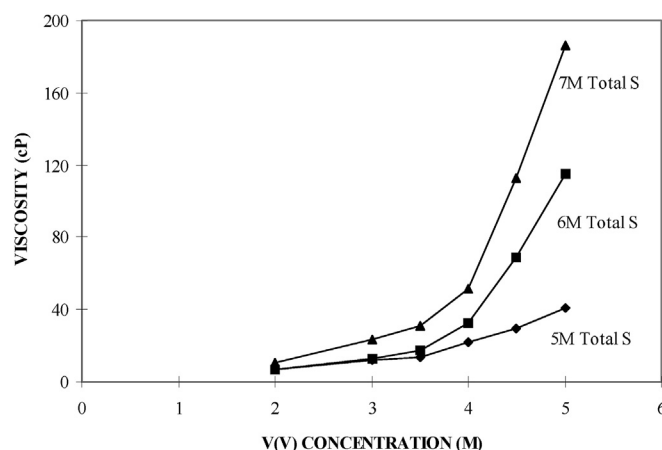


Fig. 6. Variation in viscosity of 2M–5M vanadium(V) solutions in 5M–7M total sulphate/bisulphate at 20 °C [1].

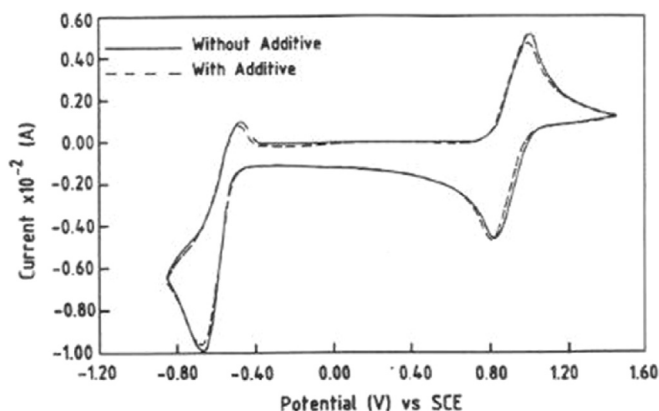


Fig. 7. Cyclic voltammogram of 4 M V(V) solution in 5 M total sulphate/bisulphate with and without additive.

species during discharge of the vanadium batteries. Until it is charged back to the V(V) state it will remain as V(IV) species and thus has to be stable under the discharged condition of the battery. The initial screening of additives for the V(IV) solution was discussed earlier, and the long term evaluation (2400 h) of 4 M V(IV) solution in 6 M total sulphate/bisulphate at 20 °C is illustrated in Fig. 8. The additive KS11 thus shows very good performance with an induction time of about 56 days and an apparent equilibrium V(IV) concentration of 3.23 M. Thus, additive formulation KS11 can prevent precipitation of both 4 M V(V) and V(IV) species in 6 M total sulphate/bisulphate for a minimum period of about 40 days without any decrease in vanadium concentration.

The negative half-cell of the vanadium redox battery contains V(II) and V(III) species in its charged and discharged state respectively. The stability of these two solutions is also equally important at similar vanadium concentrations to be able to operate the battery at high energy density.

A V(III) solution of 4 M concentration was prepared in 6 M total sulphate/bisulphate. Additive formulations KS11 and SP-L at a dose level of 2 wt% were evaluated using 4 M V(III) solution in 6 M total sulphate/bisulphate at 20 °C. The sample in which SP-L was added started to precipitate immediately. This rapid precipitation was probably due to some reaction with the PSA present in the formulation SP-L.

However, the blank V(III) solution and the V(III) solution with KS11 did not precipitate for six days. Both the samples were moved

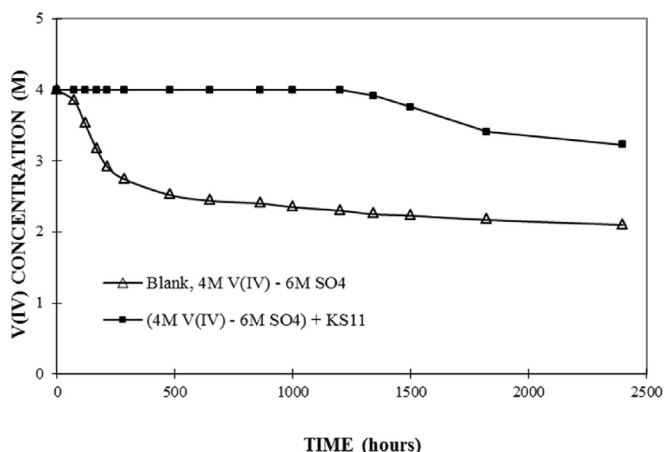


Fig. 8. Performance of KS11 to inhibit precipitation of 4 M V(IV) solution in 6 M total sulphate/bisulphate at 20 °C.

from the 20 °C water bath to a refrigerator maintained at about 3 °C. In the beginning both samples were monitored on a daily basis to visually observe the start of any V(III) precipitation. No precipitation was observed for about 1000 h, in both the blank solution as well as in V(III) solution with KS11 at 3 °C. The solutions were left in the refrigerator for a longer time with periodic monitoring. Surprisingly it was noted that both 4 M V(III) solution and 4 M V(III) solution + KS11 did not show any sign of precipitation for about three months at 3 °C.

Preliminary evaluation of KS11 was carried out by Skyllas-Kazacos and Mousa [37] to prevent precipitation of V(II) species. Encouraging results were obtained when a 2 M V(II) solution in 5 M total sulphate/bisulphate was evaluated using KS11 at 3 °C. The blank V(II) solution started precipitation after five days whereas V(II) solution containing formulation KS11 was able to hold the precipitation for 27 days, an increase in induction time by a factor of five.

It can be concluded that the formulation KS11 developed in this study has a significant potential to stabilise the supersaturated vanadium solutions of V(II), V(III), V(IV) and V(V) species at a vanadium concentration of 3.5 M in 5.7 M total sulphate/bisulphate for a period of about one month at operating temperatures between 5 °C and 40 °C.

#### 4. Conclusions

A comprehensive evaluation of various additive formulations developed in this study was carried out to minimize thermal precipitation of highly supersaturated V(V) solutions for vanadium flow battery applications. The blended formulation KS ( $K_3PO_4 + SHMP$ ) showed better performance than all other formulations evaluated using 4 M V(V) solution in 6 M total sulphate/bisulphate (4V6S) at 40 °C for 1000 h.

The variation in temperature has a significant effect on the effectiveness of the formulation KS11. The formulation KS11 can prevent the precipitation of 4V6S solution up to 40 °C for 1000 h. Further increase in temperature to 50 °C starts the precipitation of 4V6S solution after 4 days with final concentrations of 2.3 M after 1000 h.

Increasing the total sulphate/bisulphate concentration increases the stability of V(V) solutions but increases the viscosity of the solutions and also increases the precipitation potential of V(IV) species. Preliminary evaluation of formulation KS11 to inhibit precipitation of supersaturated V(II), V(III) and V(IV) solution indicated that KS11 is inhibiting precipitation of these species at lower temperatures of 5–20 °C. A solution of composition 3.5 M V(V) in total sulphate/bisulphate concentration of 5.7 M with additive formulation KS11 appears to be very attractive for a high energy density vanadium redox battery up to a temperature of 40 °C. The effect of additive addition does not influence the electrochemical behaviour of the V(V) solutions, which exhibited very similar cyclic voltammograms with additive, and without additive.

Increasing the vanadium and total sulphate concentrations above 3.5 M and 6 M respectively is expected to increase the formation of electrochemically inactive vanadium-sulphate complexes and polyvanadic species which results in increasing the vanadium solution viscosity exponentially and subsequently reducing the electrochemical reactivity.

#### Acknowledgments

This work was sponsored by the Australian Research Council. The authors acknowledge support from the Center for Refining & Petrochemicals, Research Institute of King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia and The University of

New South Wales, Sydney, Australia.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2016.11.071>.

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