VANADIUM

Removal of vanadium from contaminated wastewater

Figure 1: Picture of a vanadium mining area

Figure 2: Picture of a druse of red vanadinite-crystals

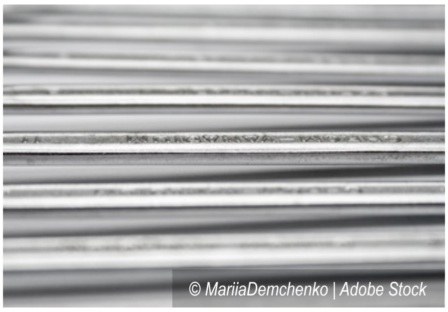

Figure 3: Picture of vanadium – a chameleon metal

Vanadium is a metal named after the Nordic goddess, Vanadis. Vanadium is ductile, malleable and corrosion resistant. Vanadium rarely occurs as a free element. It is a component in minerals such as vanadinite, carnotite, patronite and titanium magnetite. In surface and groundwater, it occurs dissolved as $[HVO_4]^{2-}$ or $[H_2VO_4]^-$ up to 100 µg/l.

Metallic vanadium is used in the steel industry, the so-called ferrovanadium is used in chromium-vanadium steels to increase toughness. Vanadium oxides, vanadium salts or vanadium solutions are used as catalysts in many processes of basic chemistry, as an active ingredient in pharmaceuticals and as an agent for coatings or in etching processes.

In addition to the intended applications, the technological process often produces wastewater contaminated by vanadium, which is toxic and suspected of acting as a mutagenic clastogen that has a carcinogenic effect in the chromosomes; therefore, it must be treated before discharge.

Figure 4: Picture of vanadium - the chameleon metal

Vanadium in wastewater

Vanadium can exist in different oxidation states, whereby in oxygenated waters and in industrial effluents the toxic 5+ vanadate anions are often present.

The Bavarian Environmental Agency has issued a permit for the discharge of vanadate 5+ contaminated wastewater into surface waters and public sewage systems, and recommends a guide value of 200 µg/l.

Generally applicable limit values could not be found at the time of the research.

[Bayerisches Landesamt für Wasserwirtschaft, Merkblatt Nr. 4.5/15 v. 25.7.2005; Merkblatt 4.5/1 v. Sept. 2014].

Oxidation states of vanadium

Vanadium can be present in compounds in various oxidation states (+5, +4, +3, +2, +1, 0, -1, -3). The most stable forms are +4 and +5.

The oxidation states can be easily distinguished by color (see Fig. 5).

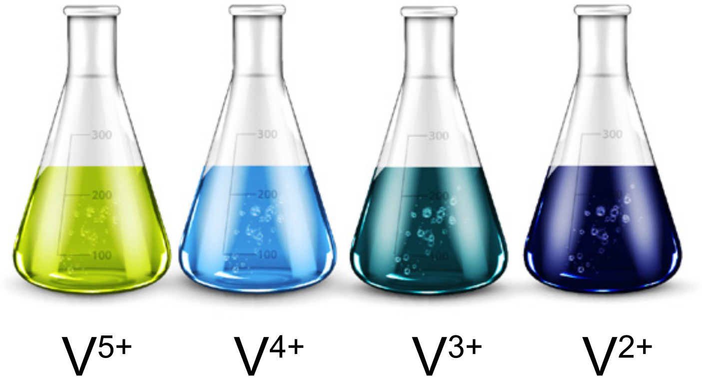

Figure 5: Colors of the vanadium oxidation stages

Vanadium Removal

Vanadium removal is based on ferro chloride/vanadate co-precipitation, where the stoichiometric molar ratio of Fe to V must be at least 1 to 3. The activation of the reaction takes place in an acidic environment and the precipitation is conducted in the alkaline milieu. The block diagram in Figure 6 shows the required chemical process steps and the respective coloration of the obtained product solution.

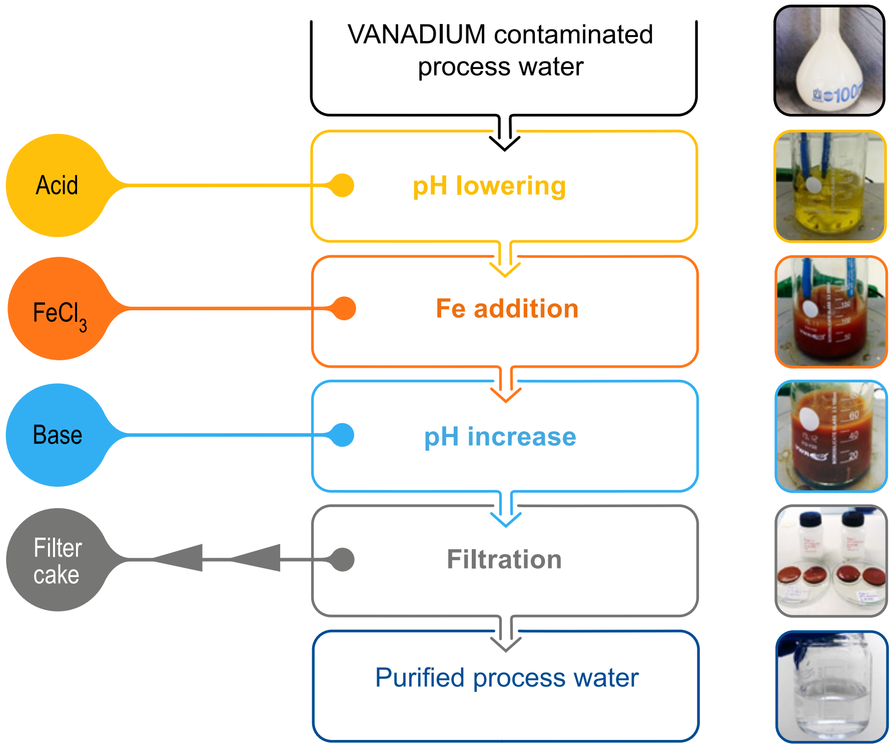

Figure 6: Block diagram of vanadium removal

Analyses

The results of the vanadium analyses show the dependence of the vanadium removal of the pH shift and the ratio between Fe to V. (see Fig. 7)

Vanadium	Fe: V ratio	Unit	Analysis
Process water (original)		mg/l	720
$FeCl_3$ - precipitation (without pH reduction)	2:1	mg/l	510
	4:1	mg/l	390
$FeCl_3$ - precipitation (with pH reduction)	2:1	mg/l	0,41
	4:1	mg/l	0,08
DIN EN ISO 17294-2: 2005-02 (analytical ceiling 0.01 mg/l)			

Figure 7: Table with analytical results

Co-precipitation theory

The chemical co-precipitation process is a special form of chemical precipitation in which the desired reagents are first brought into treated reaction solution and then mixed to obtain a homogeneous composition.

The addition of the Fe (III) chloride solution causes turbidity, where floating hydroxides and carbonates are formed.

With an increase of pH for the treated reaction solution, flocculation occurs and transforms a dissolved chemical substance (pollutant) into an insoluble solid, and then the separation of the different fractions (phases) takes place. Therefore, the precipitated sediments can be filtered mechanically and thermally concentrated. In the Pourbaix diagram (Fig. 8) the state of the wastewater in the relevant process step can be seen and classified.

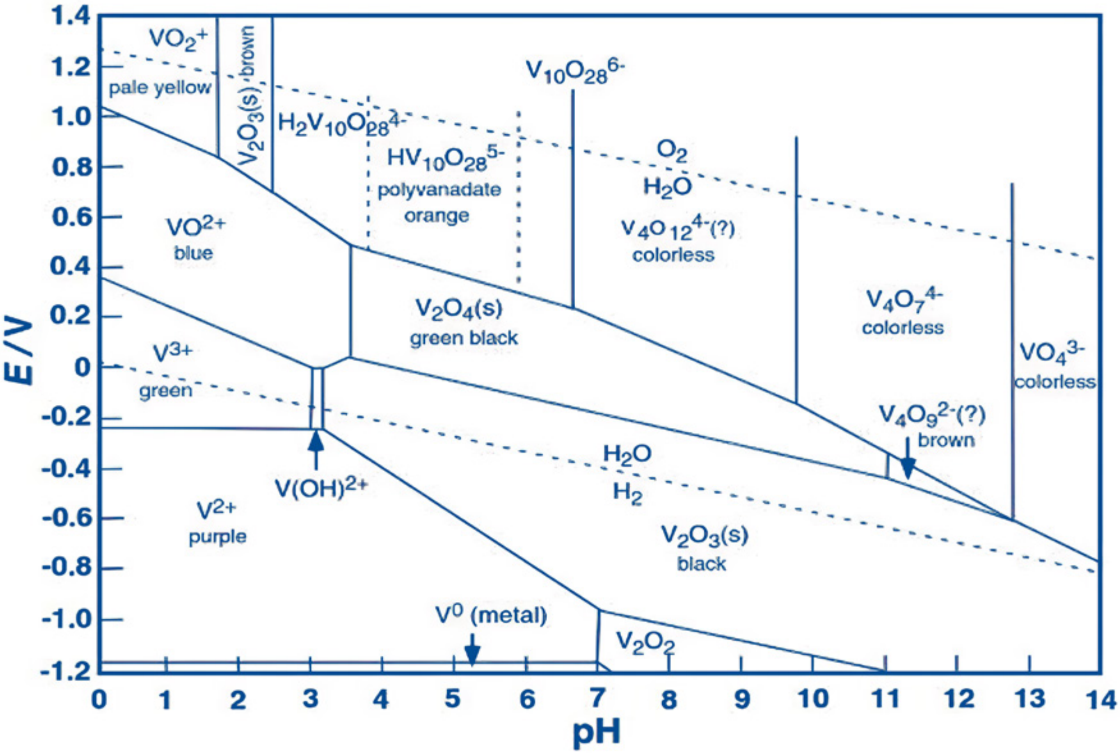

Figure 8:
Pourbaix-diagram of vanadium
[SEMANTIC SCHOLAR]

Design of a plant

The design of wastewater plants for vanadium removal can be carried out by the company “Umwelt- und Ingenieurtechnik GmbH Dresden” (UIT) based on test results with real process or wastewater in the technical center of UIT as well as expert experience and a process simulation.

Practical tests in the UIT technical center show possible over-lapping effects and help to include the upstream and downstream process steps into the plant design.

Based on these findings and the hydrochemical simulation, the optimal parameters for a large-scale treatment plant are developed. (Fig. 9)

Figure 9 - Multifunctional plant for metal separation, built by Umwelt- und Ingenieurtechnik GmbH Dresden

Plant Engineering and Construction Company

The company “Umwelt- und Ingenieurtechnik GmbH Dresden“ (UIT) offers a wide range of services conducting wastewater sampling, sample analysis and technological process evaluation of industrial wastewater streams; develops individually customized specific process solutions at its own technical center; proves process reliability using bench-scale tests; designs and constructs lab and/or onsite fully equipped pilot plants including piloting using Rack-based or Containerized concepts; designs and constructs full scale turnkey industrial and mining plants; and develops plant & application oriented automation including remote diagnostics, control, troubleshooting & monitoring. UIT develops unique solutions, engineer, construct and commission industrial process water and wastewater treatment plants.

Industrial references of this technology are executed in various applications, for example, in catalyst production plants and in metal separation in mining plants after acidic leaching.

Heavy metals, acids, salts

For many years, UIT‘s specialists have been providing expertise in the fields of process and industrial wastewater treatment, separation of heavy metals, metal extraction, and acid and salt separation.

UIT holds ownership of its developed in-house simulation software based on PHREEQC® used for system and process simulations for various practical applications to optimize chemical processes.