Process Chemistry and Acid Management for Titanium Pickling Processes

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Abstract:

Titanium is normally pickled in hydrofluoric acid and nitric acid, so called mixed acid. It is important to be able to monitor how the pickling proceeds to be able to control the addition of fresh acid and in the very common batch processing to know when the bath should be discarded. To correctly evaluate analysis data it is necessary to gain a deeper understanding of the chemistry of the pickle liquor.

As the titanium ion concentration increases by time in the pickling solution HF is consumed by formation of titanium fluoride complexes. It has been observed experimentally that the overall dissolution process of titanium is different depending on whether the F/Ti molar ratio is above or below 6. When the ratio is larger than about 6, at least momentarily TiF_6^{-2} is the dominating species in the solution and there is an excess of HF available for pickling. The formation of titanium fluoride complexes has therefore a direct impact on the pickling rate and strongly affects the economics of the process.

Within the present work the speciation in industrial mixed acid titanium pickling liquors was estimated using the chemical speciation software Medusa. Since the necessary complexes and reactions were missing in the program a new database was constructed. Conditional stability constants for the system Ti-HF-HNO_3-H_2O was gathered by performing a thorough literature review. Real production data from Titanium producers were used as input data in the calculations.

The elevated understanding of the process chemistry has let to advances in process control and a newly developed acid retardation process by Scanacon AB of Sweden. The economics, the quality and the environmental impact of the pickling process can be greatly improved. The new acid retardation process will discard Titanium with a much higher efficiency compared to the existing process as also anionic Ti-complexes can be discarded with minimal acid loss. The metal concentration whilst pickling can be stabilised at preferable levels defined by full scale process economics. Expensive discarding of acids due to high Titanium concentrations can be avoided altogether.

Keywords: Pickling chemistry, Speciation, Acid savings, Production management,

Introduction:

Experiments have shown that the pickling rate of Ti in mixed acid decreases by time. This can be due to changes in the surface layer and/or by modification of the pickling solution by time. The decrease in pickling rate can be explained by the complexation of fluoride ions by titanium (IV). As the titanium ion concentration increases by time in the pickling solution hydrofluoric acid is consumed by formation of titanium fluoride complexes. The pickling rate depends on the free concentration of HF. It has been observed experimentally that the overall dissolution processes (including complexation) are different depending on whether the F_{tot}/Ti_{tot} molar ratio is above or below 6 [1]. This behavior can be confirmed by Scanacon from experience of full scale pickling processes. Further studies of the process chemistry were needed both to describe the reaction and complexation chemistry and also to increase the knowledge for more accurate measuring and process control.

Pickling Chemistry:

Pickling of titanium in solely hydrofluoric acid is not recommended due to hydride formation at the metal surface, which causes metal embrittlement. Titanium reacts with HF according to the following formula:

$$2Ti + 6HF \rightarrow 2Ti^{+3} + 6F^{-} + 3H_2 \quad (1)$$

The trivalent titanium ions are then further oxidized by atmospheric oxygen or very slowly by HF and then complexed by fluoride ions. [1]

Pickling of titanium in solely nitric acid is not recommended due to the formation of a protective scale layer of TiO_2. Titanium reacts with HNO_3 according to the following formula:

$$Ti + 2HNO_3 \rightarrow TiO_2 + 2HNO_2 \quad (2)$$

When a mixture of HF and HNO_3 (mixed acid) is used as etch solution titanium dioxide is readily dissolved by HF:

$$TiO_2 + 6HF \rightarrow 2H^{+} + TiF_6^{-2} + 2H_2O \quad (3)$$

The exposed surface metal atoms are then oxidized according to reaction 10:

$$2Ti + 3HNO_3 + 6H^{+} \rightarrow 2Ti^{3+}_{ads} + 3HNO_2 + 3H_2O \quad (4)$$

The adsorbed trivalent titanium cations will then be oxidized either as soluble titanium fluorides by reaction 5 or as insoluble TiO_2 according to reaction 6. [1]

$$Ti^{3+}_{ads} + ½HNO_3 + nHF \rightarrow TiF_n^{(n-4)-} + ½HNO_2 + (n-1)H^{+} + ½H_2O \quad (5)$$

$$2Ti^{3+}_{ads} + HNO_3 + 3H_2O \rightarrow 2TiO_2 + HNO_2 + 6H \quad (6)$$

Higher concentrations of hydrofluoric acid will accelerate reactions 3 and 5, both which are dissolution reactions. Increased concentration of HNO_3 will accelerate the oxidation reaction 4, the dissolution reaction 5 and the passivation reaction 6. It has been found that increasing the nitric acid concentration, keeping the concentration of HF constant, first increases the etch rate until an optimum rate is obtained, then by further increasing the nitric acid concentration the etch rate starts to decrease.

Nitrous acid is unstable and when it decomposes nitrous gas evolves:

$$2HNO_2 \rightarrow HNO_3 + ½N_2O + ½H_2O \quad (7)$$

In fact a range of reduction products are formed in the reactions and different nitrous gases (NO_x) evolve.

Combining equations 4, 5 and 6 gives the overall reaction for the pickling of Ti in mixed acid:

$$Ti + nHF + HNO_3 \rightarrow (n-4)H^{+} + TiF_n^{(4-n)} + ½N_2O + 2½H_2O \quad (8)$$

The pickling process thus results in the formation of nitrous gases and titanium fluoride complexes, $TiF_n^{(4-n)}$. In solutions with an excess of HF, TiF_6^{-2} is the dominating titanium fluoride ion.

The etch rate of titanium and titanium alloys has been determined as a function of acid composition and temperature. [1,2]

Titanium Fluoride Speciation:

There are numerous programs available to facilitate modelling of speciation in different systems, e.g. visual MINTEQ, Medusa, MICROQL, PHREEQC, OLI, the Geochemists workbench (GWB) and EQ3/6. The first three can only model speciation in low ionic strength solutions (approx. <0.5M). PHREEQC includes a module to calculate activity coefficients using Pitzer parameters. OLI, GWB and EQ3/6 are commercial programs. However, none of the programs contains all the necessary parameters to calculate the speciation in spent Ti pickle solutions.

The computer program Medusa was used to model the speciation. This program makes diagrams based on the equilibrium constants given to the program. The program can correct for ionic strengths up to about 0.3M when used together with the thermodynamic stability constants. In the modelling no correction for ionic strength was made in the program and conditional stability constants were used [3,4]. Since the necessary reactions and complexes were missing in the program a new database was constructed.

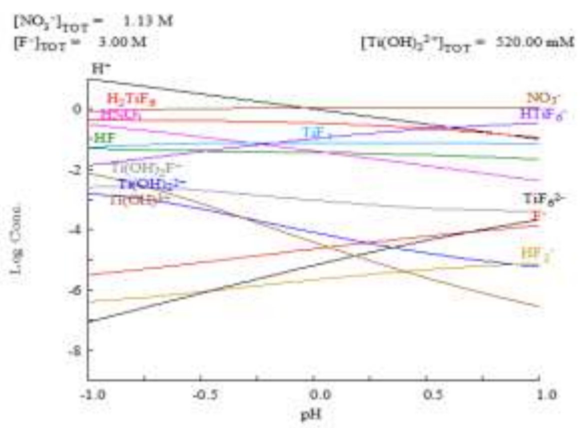

Figure 1: A typical data plot from the speciation program Medusa

Data from real pickling processes as well as different cases with varying F/Ti relationships at different HNO3 concentration were analyzed.

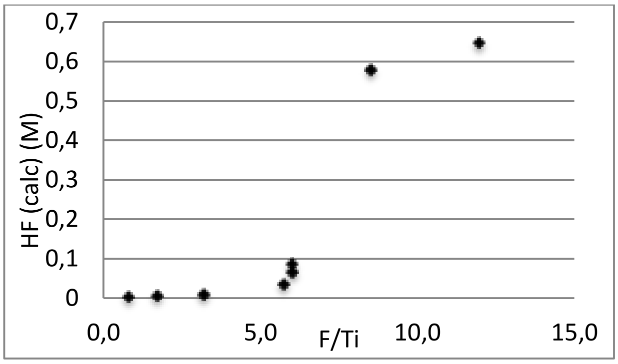

Figure 2: Free HF at different F/Ti ratios

When the ratio is less than 6 HF need to be released from the Titanium complexes in order to be available for pickling. This is further illustrated by Table 1. At high ratios TiF_6^{-2} is the dominant Titanium specie and excess fluoride will exist as free HF. At low ratios all fluoride is complexed with Titanium and the dominant species is TiF_4

Table 1: Distribution of fluoride at different F/Ti molar ratios

Ratio (F/Ti)	HF (%)	TIF_6^{-2} (%)	TiF_4 (%)
12	53	47	0
6	2	96	3
2	1	18	81

As the ratio will constantly change due to titanium dissolution and acid addition the pickling process efficiency will vary over time. Scanacon has noticed that industrial pickling processes often are operated at an initial high ratio (above 6) which is then decreased (below 6) as the process proceeds.

Conclusion:

From the speciation it can be concluded that the concentration of free HF or free fluoride is negligible in the pickling bath when the relation F/Ti is below the value of 6. The pickling reaction will continue while fluoride is released from the titanium fluoride complexes, however at a lower rate. When the value is too low the reaction will cease. Precipitation of a solid phase of Titanium oxide occurs.

It can be seen that free HF as often used to describe or govern a pickling process does not exist at low F/Ti values. The description active HF or available HF has to be introduced to describe the reaction.

As it has been observed by Scanacon many pickling process are operated at varying F/Ti relation, normally above 6 when the process is started and below 6 when operation is seized and the acid is discarded. If this occurs it can be concluded that less HF has been dosed during operation compared to the HF consumed by the reactions.

A stable process with a constant Titanium concentration and more predictable F/Ti relation is the more favourable mode of operation.

Industrial implication:

The speciation and the information gained on the chemistry of the Titanium pickling process will be used to describe the process more accurately. The relation of F/Ti governs the pickling efficiency and it can be shown that a stable process with fixed Titanium concentration is favourable compared to the batch mode of operation. The data allows to draw conclusion on acid dosing required for a fixed process efficiency at stabilized Titanium levels.

The data has helped Scanacon to improve the existing retardation technology. The new process takes into account the formation of anionic titanium fluoride complexes (TiF_5^-; TiF_6^{2-}). In the newly engineered system higher acid recovery as well as Titanium separation efficiencies can be achieved. With this, the process can be stabilised at defined concentrations and operated in a continuous mode. Together with the end user the pickling efficiency can be described more accurately. Process quality can be improved, acid consumption and negative environmental benefits such as nitrate discharge can be reduced.

The speciation of the Titanium fluoride has great implication on how to monitor the process and advances in computing the measured acid and titanium values have been made.

Future work:

Work is in progress for identifying the solid phase(s) precipitating from spent acid pickling baths by XRD-spectroscopy and determining the solubility of said precipitate in mixed acid at industrially relevant processing conditions. The speciation will also be determined by fluoride NMR-spectroscopy to validate the speciation calculations and gain further insight into the titanium speciation (e.g. kinetics) in mixed pickle acid. The long term aim is to further improve acid recycling for Titanium pickling processes and propose a possibility for Titanium recovery.

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Process Chemistry and Acid Management in Titanium Pickling Processes

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Process Chemistry and Acid Management in Titanium Pickling Processes

- Process Chemistry
  - Pickling Chemistry
  - Complex speciation
- Acid Management
  - Mode of operation
  - Acid Consumption
  - Quality, Environmental, Financial aspects

Process Chemistry

Titanium is normally pickled in hydrofluoric acid (HF) and nitric acid (HNO_3) , so called mixed acid.

The main reactions are the dissolution of Titanium oxides formed during heat treatment and base metal dissolution to acquire the desired surface properties.

Acid concentration, agitation, dissolved metal concentration and temperature all effect the rate of pickling and final product quality.

The nitric acid acts mainly as an oxidation agent and lowering the pH.

The hydrofluoric acid dissolve the possible oxide layer and acts as complexing agent of free Titanium in the solution.

Process Chemistry

The main reactions can be summarized

For oxide dissolution:

$TiO_2 + 6HF \rightarrow 2H^+ + TiF_6^{-2} + 2H_2O$

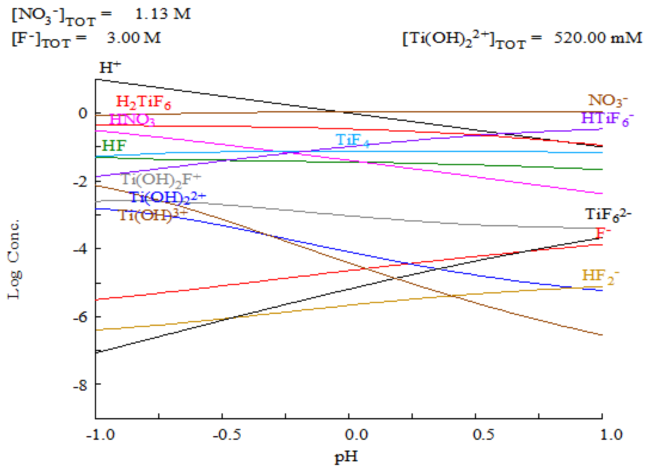
For Titanium pickling:

$Ti + nHF + HNO_3 \rightarrow (n\text{-}4)H^+ + TiF_n^{(4-n)} + ½N_2O + 2½H_2O$

From this equation it can be seen that the relation ship of HF/Ti is governing the speciation of the complexes and ultimately the pickling efficiency.

HF/Ti speciation

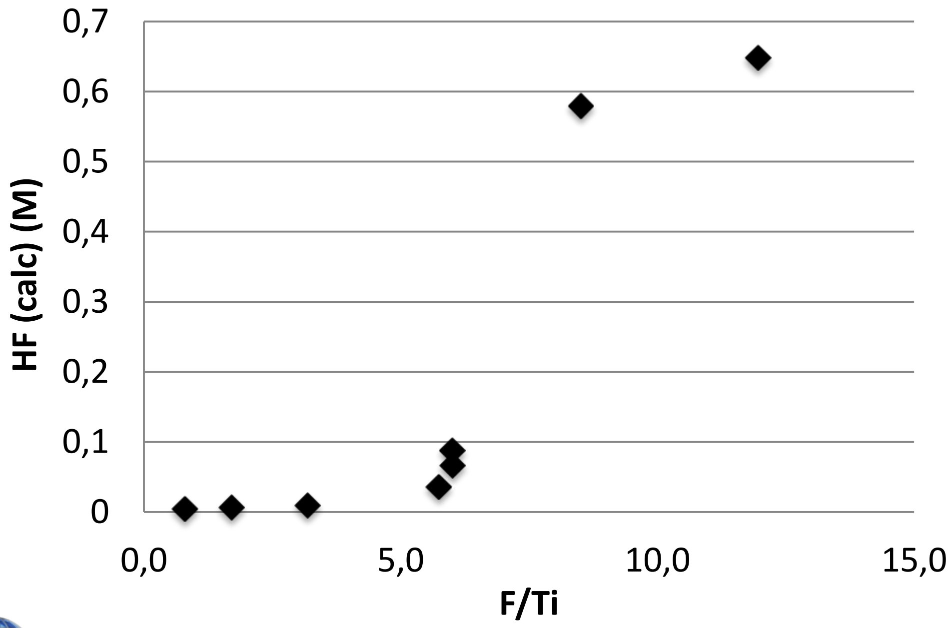
The speciation of a pickling system was simulated using the software Medusa, using different equilibrium constans for the system of Ti-HF-HNO3-H2O.



Data from real pickling processes as well as different case with varying HF/Ti relationships at different HNO3 concentration were analysed

HF/Ti speciation

Example: Availability of free HF in the pickling system



The diagram visualises the non existance of free HF at low F/Ti ratios.
The pickling reaction is driven forward by the reaction H_2TiF_6 -> $HTiF_5$ +HF -> TiF_4 +HF -> … TiO_2
This releases HF, however the pickling rate is lowered

HF/Ti speciation

Example: Distribution of Fluoride at different total F/Ti molar ratios in %

Ratio (F/Ti)	HF	TiF_6^{-2}	TiF_4
12	53	47	0
6	2	96	3
2	1	18	81

HF/Ti speciation

Summary of findings:

- Titanium can form complexes with up to 6 fluoride ions according to: $(n-4)H^{+} + TiF_{n}^{(4-n)}$
- The F/Ti ratio influences the pickling rate.
- No free HF exists if the ratio is low. The pickling process has to be described by active HF.
- The pickling rate is lowered and eventually there is a risk of precipitation.
- Due to the titanium dissolution and acid addition the ratio is constantly changing leading to varying process conditions.

HF/Ti speciation

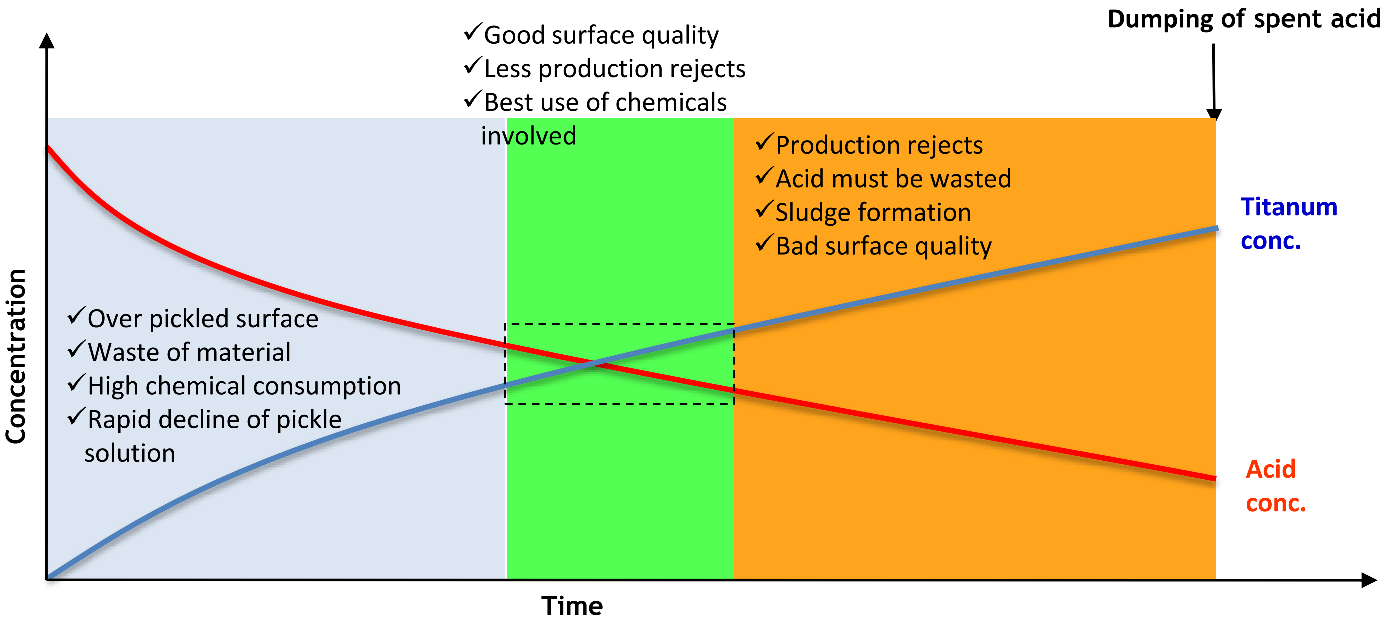
Industrial implication

or:

What does it all mean?

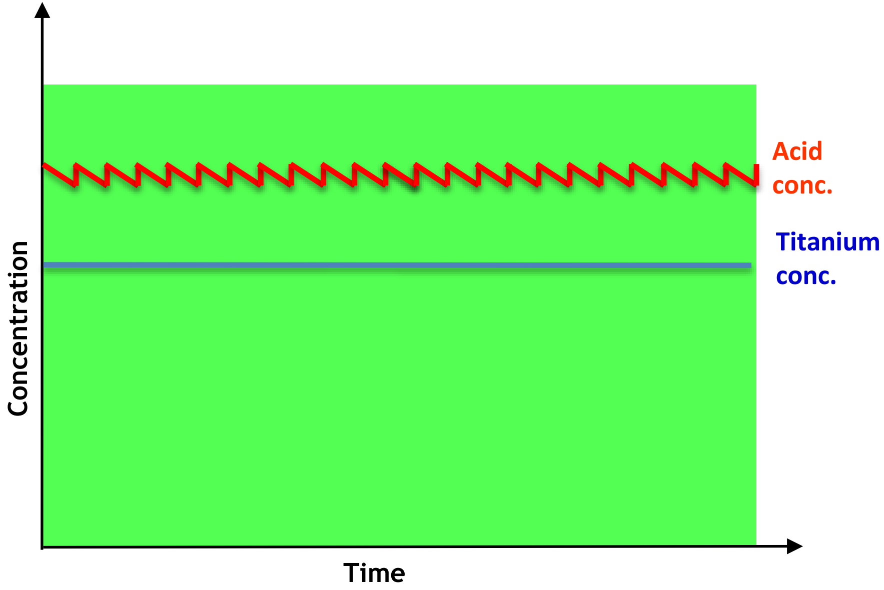
Process Management

Titanium pickling processes are often run as batch processes where pickling effect and product quality vary over time. Production time loss at end of cycle due to stand still.



Process Management

A continuous process with stabilized acid and titanium concentration can guarantee the best possible production outcome.



Acid analysis are performed in close intervals, dosing performed and stable conditions guaranteed.

The Titanium concentration can be kept a steady level as an acid retardation can discharge Titanium at the same rate as the build up in the process. Due to the high efficiency separation process acid is recovered and reused to a very large extend.

Process Management

What does it mean for Scanacon

With knowledge from the process chemistry study the Scanacon acid retardation systems could be greatly improved due to the higher understanding of the anionic behaviour of TiF complexes.

The process control and measuring of the pickling process can be described in much more accurate way.

Process Management

What does it mean for the Titanium production route

With the newly engineered acid recovery system, the pickling process can easliy be kept with a define operating window in continuous operation. This favours a stable process, repeatable quality and reduced process downtime.

Acid loss is drastically reduced due to (improved) acid recycling, fresh acid purchase as well as impact to the environment e.g. discharge of nitrates are cut down in the same manner as waste volumes

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by newly improved separation
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Thank you for your attention