

# Titanium in Chlorate, Chloralkali and Chlorine Dioxide Applications

An overview of where Ti use is essential or optional, what alternative materials are used. Advantages and disadvantages, type of corrosion, which may occur.



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# ERCO Worldwide

ERCO Worldwide has operated for over 100 years, focused largely on the production and supply of inorganic chemicals along with technology for the generation of chlorine dioxide. ERCO's major business areas include sodium chlorate, chlor-alkali chemicals, sodium chlorite, and chlorine dioxide technology. Chlorine dioxide technology is environmentally preferred for the pulp and paper industry.

ERCO Worldwide's chloralkali business serves a variety of industries including municipal and industrial water treatment, food processing, fertilizers, airport de-icing, and oil and gas.

ERCO Worldwide is the second largest producer of sodium chlorate in the world. It has the world's largest installed base of modern chlorine dioxide generators and related technology and is the second largest producer of potassium chemicals in North America.



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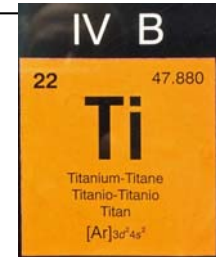
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# Some Facts About Titanium




- Named after the Titans, Greek gods of myth;
- Titanium is a chemical element with symbol Ti, atomic number 22 and atomic weight 47.88.
- It is a shiny transition metal with a silver color, low density, and high strength.
- It's as strong as steel, but only 50% the weight.
- It has outstanding corrosion resistance.
- Titanium is nontoxic and biocompatible, considered as the medical metal of choice.
- Titanium – a true titan of technology!



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# Ti Corrosion Resistance

- Highly resistant to corrosion because of the formation of stable, self healing oxide.
- Immune to all natural environments
- Resist corrosion in oxidizing, neutral and inhibited reducing conditions
- Fully resistant to wet chlorine, chlorine dioxide, hypochlorite
- Does not stress-crack in most conditions
- Resists erosion-corrosion in seawater with solids



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# Ti Resistance Limitations

- Severely attacked in acidic fluoride environment.
- Susceptible to crevice corrosion in very hot chloride solutions.
- Not compatible with some fluoroelastomeric gaskets.
- Susceptible to hydrogen embrittlement.
- Corrode in acids (HCl, H<sub>2</sub>SO<sub>4</sub>).
- Attacked by hot caustic (> 18 wt. %, temp.>60°C).
- Attacked by dry chlorine.
- Stress-crack in anhydrous methanol mixed with acidic chlorides.
- Attacked by some organic acids
- Attacked by alkaline hydrogen peroxide



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# Titanium Grades

- ASTM B265 Specification for Titanium and Titanium Alloys Strip, Sheet, and Plate lists **39 grades** of titanium
  - Unalloyed titanium:  
high purity Ti or electrolytic Ti  
ASTM Grades: 1, 2, 3, 4
  - Modified titanium  
Palladium ASTM Grades: 7, 11, 16, 17  
Ni, Mo ASTM Grade 12  
Ruthenium ASTM Grades: 26, 27
  - Other grades: alpha, near-alpha alloys, alpha-beta alloys, beta alloys



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# Common Chemical Ti Grades

ASTM Grade	ALLOY	Cost Factor vs. grade 2	Main Characteristic	Resistance	Main Use
1	Ti	1.1	Formability	Nominal	electrodes
2	Ti	1.0	Strength	Nominal	tanks, piping
7	0.12-0.25 Pd	1.9	Strength	Crevice corrosion	flanges
11	0.12-0.25 Pd	2.0	Formability	Crevice corrosion	plate heat exchangers
16	0.04-0.08 Pd	1.3	Formability	Crevice corrosion	plate heat exchangers
17	0.04-0.08Pd	1.4	Strength	Crevice corrosion	flanges



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## Chlorate, Chloralkali and Chlorine Dioxide Applications

	Type of process	Corrosive chemicals	Use of titanium	Other materials
<b>Sodium chlorate</b>	Electrochemical	Chlorine (wet), sodium hypochlorite, hydrochloric acid, caustic, salt, hydrogen peroxide	Very extensive	PVDF, ECTFE, FRP, stainless steel 316 and higher grades, special grade of carbon steel
<b>Chloralkali</b>	Electrochemical	Chlorine (wet, dry), hydrochloric acid, caustic, salt	moderate	PVDF, ECTFE, PFA, FRP, PP, high grade stainless steels, nickel alloys
<b>Chlorine dioxide</b>	Chemical	Chlorine dioxide, sulfuric acid, methanol, hydrogen peroxide	Very extensive – no substitute possible	PVDF, ECTFE, PFA, FRP



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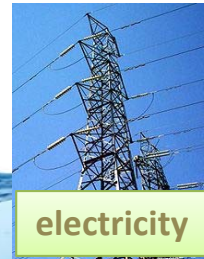


# Principle of the chlorate synthesis

- Most of chlorate is manufactured by the electrolysis of sodium chloride solution in electrochemical cell without diaphragms



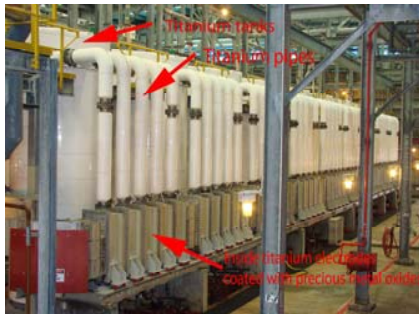
- Chlorine and sodium hypochlorite are very corrosive byproducts



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# Ti in Chlorate Plants



Equipment	Titanium	Alternative
Electrolyzer's body	Yes	Special steel
Anodes	Yes	None
Piping	Yes	Various fluoropolymers
Reactors	Yes	Various fluoropolymers
Heat exchangers	Yes	None

# Piping in Electrochemical Plant

Challenge in chlorate and chloralkali plants: current leak trough piping between electrolyzers

## Titanium

- Electrical conductivity is disadvantage
- Risk of corrosion due to excessive potential between pipe sections



## Non-Metallic

- Non conductive material offer big advantage and simplifies design



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## Stability of Passive Layer: Titanium pipe corrosion due to potential shift



Titanium corrosion resistance depends on the oxide film. In a sea water solution, the film is stable in the passive region -2 to +10V (vs SCE).



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# Galvanic Corrosion

- Titanium is highly corrosion resistant, and will usually cause more rapid damage to a less resistant active material to which it is coupled. Titanium usually will be the more noble metal and is the cathode in the galvanic cell.
- Titanium should not be coupled directly to less noble metals, such as carbon steel.
- Titanium coupled with stainless steel can make it prone to localized corrosion: crevice corrosion or pitting corrosion.



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# Crevice Corrosion

## Problem

1. Very likely in hot (> 80°C) chloride containing solutions.
2. Under some gaskets.



## Solution

1. Upgrade to palladium grade, or apply special protective coating.
2. Change to compatible gasket.
3. Consider non-metallic material



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# Titanium vs Special Alloys in Chlorate Plants

## Titanium

- Full corrosion resistance in presence of wet chlorine or hypochlorite.
- Traces of titanium in a solution have no impact on the process

## Superaustenitic and Nickel-Based Alloys

- Hastelloy C in sodium hypochlorite has corrosion rate 0.005-1.2 mm/yr depends on the conditions, which can result in nickel release into the solution.

Nickel traces are firmly restricted in the chlorate electrochemical process. Use of stainless steel various grades limited to areas where chlorine or hypochlorite are not present.



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# Scrubbers with Caustic



## Problem

- When scrubbers are operated with hot caustic (> 18 wt.%) at temp. >60°C titanium is affected by corrosion-erosion.

## Solution

- Change operating conditions to lower caustic concentration or higher oxidizer presence or
- Change titanium to non-metallic material (ECTFE, PFA)

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# Ti Corrosion by Caustic



In caustic scrubber conditions titanium can be subjected to corrosion-erosion when the combination of the following conditions exist:

- $\text{NaOH} > 18\text{wt}\%$
- Temperature  $> 65\text{C}$
- $\text{NaOCl} < 0.5 \text{ g/L}$
- High velocity areas such as pumps, elbows or where direct nozzle stream hits the surface.

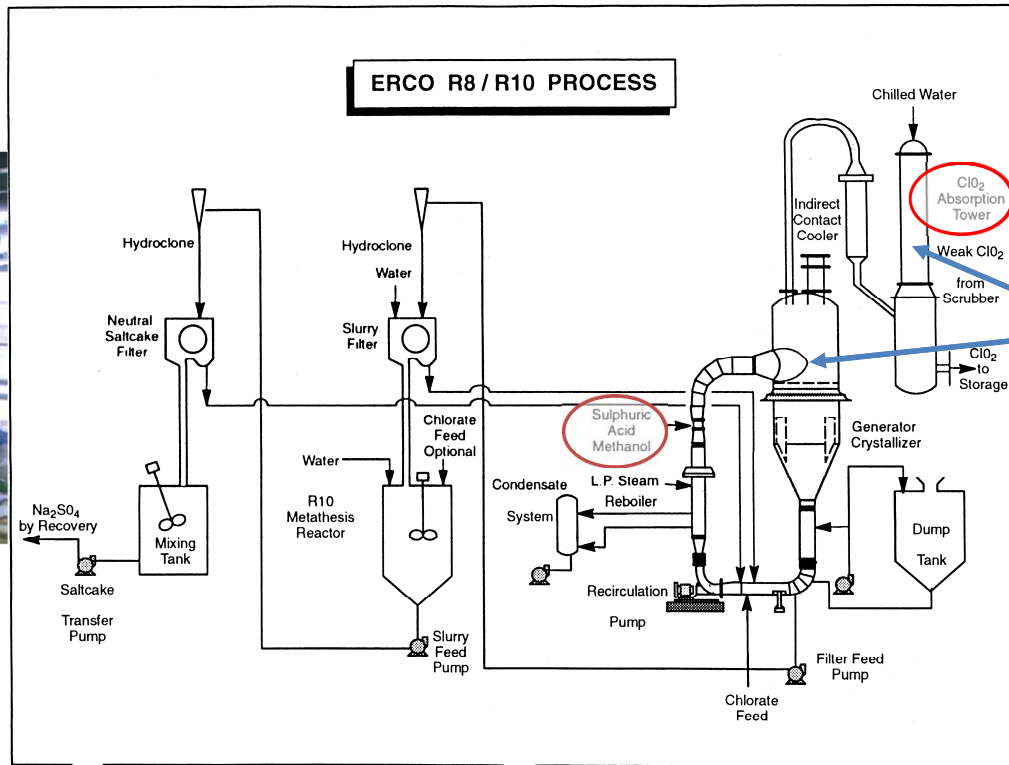


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# Titanium in Chlorine Dioxide Generation



Titanium is the only fully resistant material



# Cost of piping project Ti vs ECTFE

## Titanium piping

- Cost summary

DESCRIPTION	X	Total Cost
Total Miscellaneous Costs	\$215,538.00	
Piping Total	\$502,213.00	
Cost for Material	\$88,993.33	
Labor Total	\$384,467.00	\$1,191,211.33

## Fluoropolymer piping

- Cost summary

DESCRIPTION	Y	Total Cost
Total Miscellaneous Costs	\$205,000.00	
Piping Total	\$502,213.00	
Cost for Material	\$51,520.67	
Labor Total	\$384,467.00	\$1,143,200.67

Example of calculations for the replacement piping from old non-metallic to X – titanium or Y – ECTFE fluoropolymer. Miscellaneous cost include engineering, freight, disposal of old piping. Depends on the equipment design, proportion of one to the other can be different.

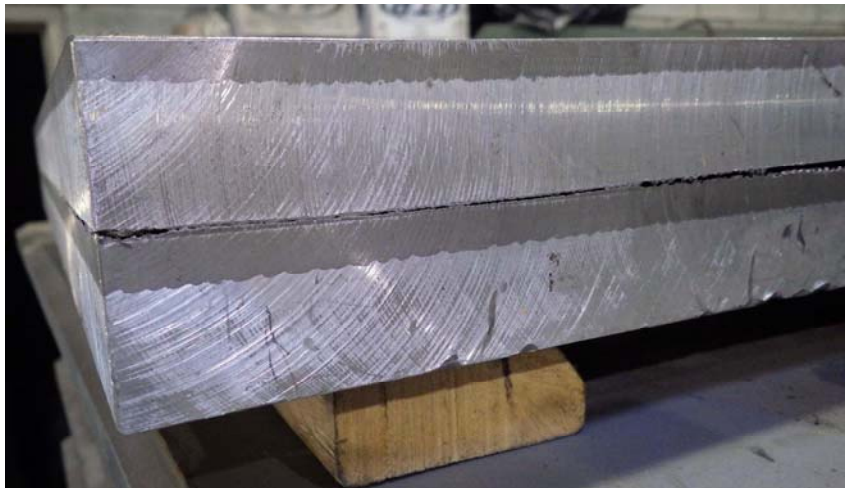


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# Titanium Clad Option



- Clad may be an option to reduce cost of the equipment.
- Titanium can form clad with steel, copper, aluminum.
- It is used to enhance properties: Ti/Cu or Ti/Al to improve electrical conductivity.



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# Titanium vs Nonmetallic

Factor	Titanium	Non-metallic
Cost of material	High	Lower or similar
Cost of equipment	Cost depends on the equipment complexity. It may be equal or marginally more expensive	Generally expected to be lower.
Fabrication and quality	Well established and consistent	More challenging to achieve consistent product
Permeation of gases and vapours	None – advantage	Through most polymers it is high, which affects equipment longevity
Longevity	Very long (> 30-50 yrs)	10 to 20 yrs
Tolerance to impurities	Some impurities (fluoride) are very limited	More tolerance
Electrical conductivity	May be disadvantage in electrochemical applications	Advantage in electrochemical applications
Recyclable, environmental	Fully recyclable	In most cases not recyclable



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# Conclusions

- Titanium offers unmatched advantages in the applications with aggressive chemicals such as wet chlorine, hypochlorite and chlorine dioxide.
- It has some limitations, which can be avoided with Ti grade selection or some process modification or special surface preparation.
- In some electrochemical applications, non-metallic (fluoropolymers) are a better option.
- In some process conditions (chlorine dioxide generation) there is no substitution to titanium.



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