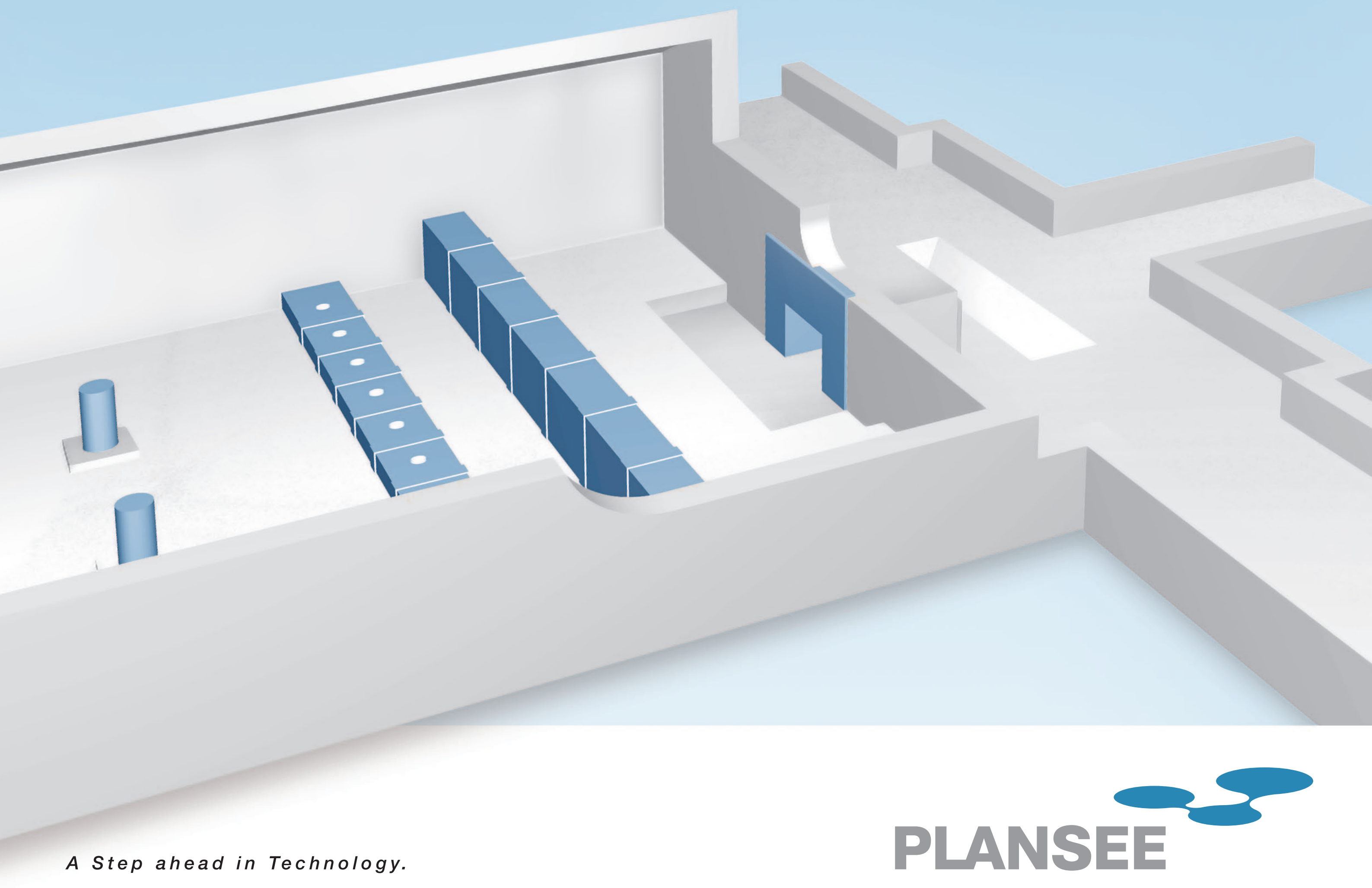
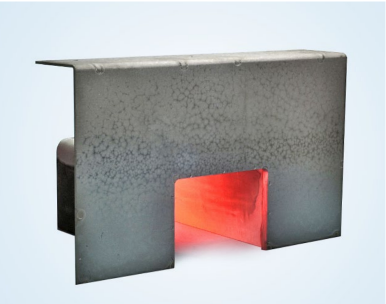
# Glass Tank Reinforcements



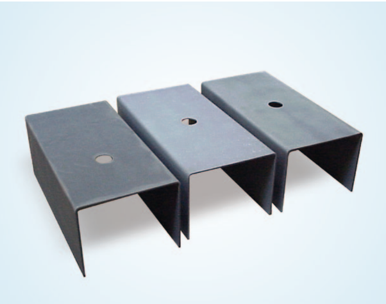
*A Step ahead in Technology.*

PLANSEE is the world market leader in powder metallurgically processed refractory and special metals. Based on the latest technologies we have been manufacturing products made from molybdenum, tungsten, tantalum, niobium, chromium and their alloys for more than 85 years. Our profound know-how regarding applications in the glass industry ensures that we can always provide the most innovative solutions for our customers.

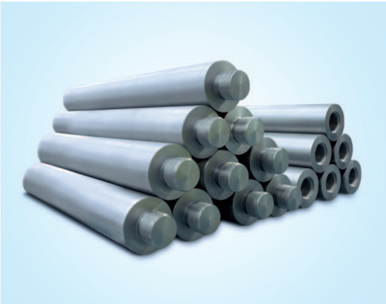
For glass production PLANSEE offers innovative glass tank reinforcements for corrosion protection as well as glass melting electrodes, homogenizing and gobbing stirrers with molybdenum core, and molybdenum and tungsten nozzles for fiber production. SIBOR®-coated molybdenum glass tank reinforcements from PLANSEE can increase service-lives of tanks while ensuring a constant glass quality. Our components are used in the most advanced glass-making processes.



Glass tank reinforcements



Crosswall / bubbler reinforcement



Glass melting electrodes

# Our contribution to efficient glass melting

When it comes to purity of material, creep-resistance and fast product availability, PLANSEE molybdenum meets the very highest demands of the glass industry. High-quality glass production requires top-performance materials. Whether you opt for standard or for specially customized dimensions and design, PLANSEE products provide you with:

- maximum purity of materials
- guaranteed oxidation-protection through SIBOR®-coating
- high corrosion-resistance
- optimized creep-strength
- reliable and certified quality inspection
- fast delivery from stock for standard products
- solutions individually tailored to each customer, with special fabrication and design capabilities

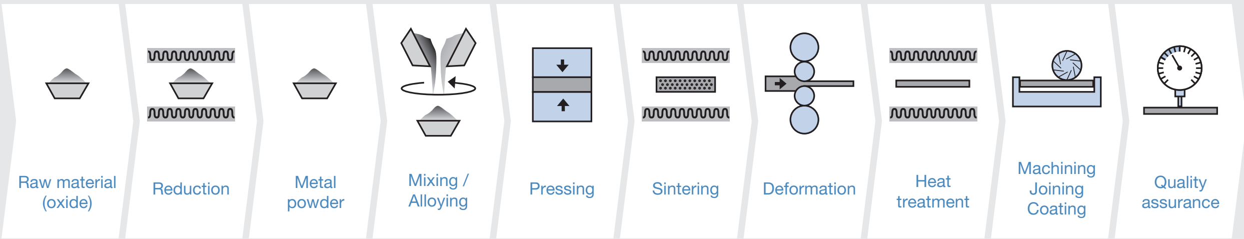
## Maximum purity

PLANSEE molybdenum stands out by reason of its high degree of purity. We guarantee a purity of 99.97 %, the typical purity is even higher (99.99 %). Traces of impurities such as carbon, nickel and iron can lead to bubble formation or discoloration of the glass melt. PLANSEE sets up the manufacturing process with pure molybdenum oxide, without any recycled scrap. By manufacturing entirely in-house – from the conversion of oxide into metallic molybdenum powder, through to pressing, sintering, deformation, and finishing – PLANSEE guarantees the highest quality available.

Chemical specifications for molybdenum products

| Element | Guaranteed analysis max. [μg/g] | Typical analysis max. [μg/g] | Element | Guaranteed analysis max. [μg/g] | Typical analysis max. [μg/g] | Element | Guaranteed analysis max. [μg/g] | Typical analysis max. [μg/g] |
|---|---|---|---|---|---|---|---|---|
| Ag | 10 | < 5 | Fe | 60 | 30 | P | 20 | < 10 |
| Al | 10 | < 5 | H | 10 | 3 | Pb | 10 | 3 |
| As | 5 | 1 | K | 10 | 3 | S | 10 | < 2 |
| Ba | 5 | < 1 | Mg | 10 | < 5 | Si | 30 | 5 |
| C | 30 | 15 | Mn | 2 | < 1 | Ta | 20 | < 10 |
| Ca | 20 | 5 | N | 5 | < 2 | Ti | 10 | 2 |
| Cd | 50 | < 2 | Na | 10 | < 2 | W | 250 | 100 |
| Co | 20 | 3 | Nb | 10 | < 5 | Zn | 10 | < 5 |
| Cr | 20 | 3 | Ni | 10 | 5 | Zr | 10 | < 2 |
| Cu | 20 | 5 | O | 40 | 15 | Mo | min. 99.7 %* | 99.99 %* |

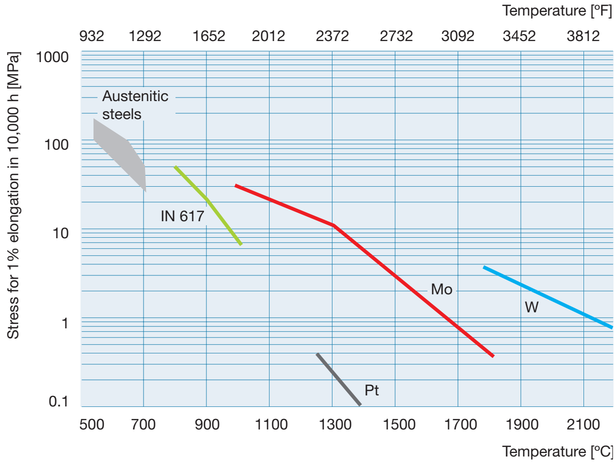
**) Metallic purity without tungsten*




Schematic process for the production of molybdenum products

## Material properties of molybdenum

Molybdenum, like other refractory metals, is distinguished by its impressive properties at high temperatures. It is used when conventional metals such as iron, copper, nickel and aluminium are no longer suitable for particular applications. Due to the beneficial mechanical, physical and chemical high temperature properties, molybdenum is widely used in the glass industry where temperatures in the range of 1100 °C / 2012 °F to 1700 °C / 3092 °F are reached, especially in the areas of the melting tank and the feeders.




Creep-resistance of molybdenum compared to other materials

| Physical properties of molybdenum | | |
|---|---|---|
| Testing temperature | 20 °C / 68 °F | 1000 °C / 1832 °F |
| Melting point [ °C / °F] | 2620 / 4748 | |
| Density [g/cm³] | 10.2 | - |
| Thermal conductivity [ W/mK] | 141 | 113 |
| Specific electrical resistance [Ω mm²/m] | 0.056 | 0.315 |
| Av. specific heat (20 °C / 68 °F to temp.) [J/kg K] | 254 | 303 |
| Av. linear thermal expansion (20 °C / 68 °F to temp.) [1/K] | $5.15 \times 10^{-6}$ | $5.84 \times 10^{-6}$ |
| Emissivity (ground surface) | 0.06 | 0.16 |
| Vapor pressure [mbar] | $2.5 \times 10^{-6}$ (1500 °C / 2732 °F) | |
| Young's modulus [GPa] | 320 | 270 |

Unprotected wall after taking down the tank

Unprotected throat area after taking down the tank

# Glass tank reinforcements – a step ahead in technology

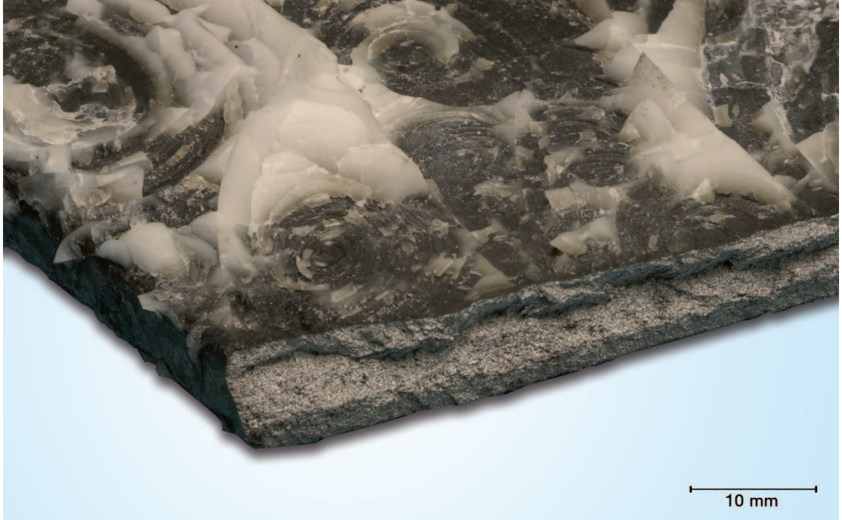
## Corrosion and wear effects in the glass tank

During the course of a glass tank's service life, the refractory bricks in the critical areas such as the doghouse, wall, bubbler and throat tend to be severely attacked by the glass melt. This attack occurs both in the form of the abrasion and erosion of the refractory bricks caused by the constant flow of glass at high temperatures and in the form of chemical corrosion caused by the glass melt itself. The damage done to the wall, bubbler and throat highly affects the flow patterns in the tank, the quality of the glass produced and finally the duration of the entire furnace campaign.
The only indication of this problem is deterioration in the glass quality and it cannot be rectified hot without draining the glass. The damage shown in the pictures is an example of severe corrosion in the areas mentioned, which was clearly visible after the tank was taken down.

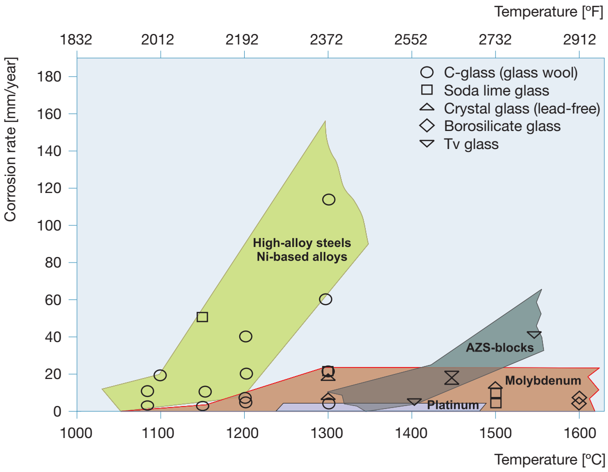
## Resistance of molybdenum to corrosion by glass melt

As tested over a wide temperature-range and in many different types of glasses, the attack of the glass melt on molybdenum is significantly less virulent than on the refractory bricks under the same conditions. Even above 1600 °C / 2912 °F the corrosion-rate hardly increases. Refractory bricks, however, show accelerated wear with increasing temperature. In addition to the material's excellent creep and chemical resistance, molybdenum protectives can reduce the amount of small particles or larger stones washed into the glass melt from the refractories. This also minimizes abrasion damage to parts further down the production line such as stirrers, gobbing stirrers or cutting knives.

Since molybdenum corrodes very slowly, there is no danger of discoloration of the glass melt. Its outstanding high-temperature strength, especially in comparison to platinum, allows large complex parts to be designed as self-supporting structures without harmful deformation at temperatures ranging from 1200 °C / 2192 °F to 1700 °C / 3092 °F.




Molybdenum protection sheet after two years service in an opal glass tank

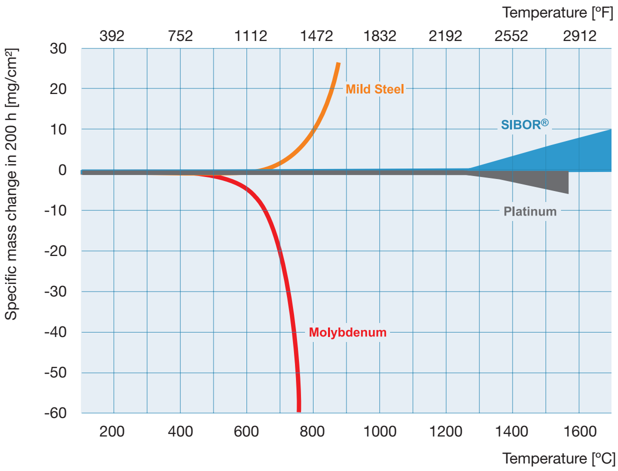



Molybdenum is characterized by its excellent corrosion-resistance to most glass melts

Compared to the equally corrosion-resistant platinum, molybdenum offers the more cost-effective solution and, in combination with SIBOR® coating, it is an ideal material for protecting highly-stressed refractory bricks in the glass tank. The SIBOR® coating reliably inhibits oxidation-damage to molybdenum at temperatures up to 1700 °C / 3092 °F. This means that today it is possible to install molybdenum components in a cold glass tank, without further measures such as covering the components with glass cullet, using a protective gas atmosphere or coating the parts with a ceramic layer. Prior to the development of SIBOR®, there was a danger that molybdenum parts, including glass melting electrodes, might sublimate partially or completely during the heating-up of the tank.

# SIBOR® – an oxidation-protective coating for molybdenum

The SIBOR® oxidation-protective coating for molybdenum is applied by atmospheric plasma spraying with subsequent heat treatment. Its outstanding characteristics are the excellent oxidation-resistance up to 1700 °C / 3092 °F and the easy handling with reduced risk of the coating to get damaged.

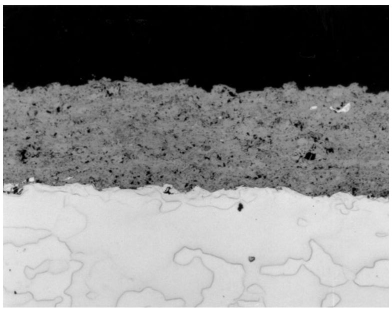



Comparison of the oxidation-resistance of various materials

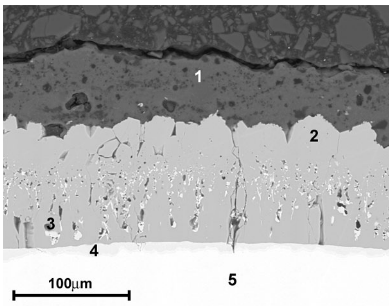
## Guaranteed oxidation protection through SIBOR® coating

Above 400 °C / 752 °F molybdenum starts to react with oxygen, forming $MoO_3$, which sublimates at higher temperatures as yellow smoke. During the up-tempering of the glass tank the SIBOR® coating reliably protects the electrodes against any oxidation. It adheres inseparably to the molybdenum by building a diffusion zone on the molybdenum surface. SIBOR®-coated glass tank reinforcements can easily be installed in a new or rebuilt tank. For further applications please refer to the PLANSEE SIBOR® brochure.

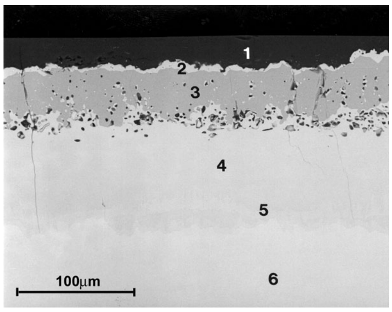
The coating consists basically of Si and B, i.e. constituent elements of glass, and it dissolves as soon as the component comes into contact with glass. It causes no discoloration or contamination whatsoever as it dissolves. SIBOR® is applied with a thickness of approximately 150 - 180 µm and forms a diffusion layer with a glass-like surface film during the heat treatment.
The pictures below show the SIBOR® layer as applied, in the annealed state with the diffusion zone and surface sealing and after an oxidation test. Such tests simulate the up-tempering procedure of a glass tank up to temperatures of 1450°C / 2642°F with subsequent isothermal soaking in an atmosphere containing oxygen.



Micrograph of a cross-section of as-coated SIBOR®, thickness 150 µm




SEM (BS-mode) of a heat-treated SIBOR® coating; EDX: 1 - Si (molten SIBOR®); 2 - Si, 4 - Mo, (Si); 3, 5 - Mo




SEM (BS-mode) cross-section of an oxidized SIBOR®-coated Mo-sample (168 h in air at 1450°C). EDX: 1 - SiO2; 2 - Mo, Si; 3 - Si, Mo; 4 - Mo, Si, B; 5 - Mo, (Si); 6 - Mo

Atmospheric plasma spaying process

## No oxidation, no discoloration, no contamination

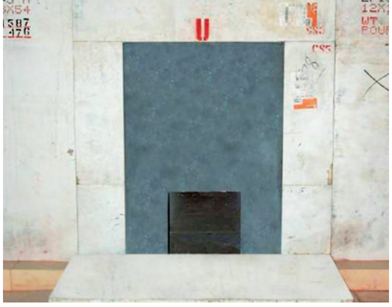
For SIBOR®-coated parts PLANSEE guarantees the following isothermal service lives in oxidizing atmospheres: 5000 h at 1250 °C / 2282 °F, 500 h at 1450 °C / 2642 °F, 50 h at 1600 °C / 2912 °F.

The heat-treated SIBOR® coating has a matt-to-shiny-silver surface appearance, is easy to handle, and does not have a tendency to flake off like ceramic coatings. After the tank has been successfully up-tempered and the SIBOR® layer is submerged, it dissolves in the glass melt. In general some bubbling may occur in the first hours. Its duration and intensity is affected by the glass composition. Since the components of the coating are basically the same as those of the glass (silicon and boron), the dissolved elements of the coating are not detectable in the glass melt.

The oxidation-resistance of the SIBOR® coating allows the user to install the SIBOR®-coated components in a cold glass tank and heat up to the working temperature without concern about safety risks. Even the slow up-tempering rates necessary to reach this temperature pose no problem for the durability of the coating. The molybdenum remains protected against oxidation by the SIBOR® layer during this time, despite the oxygen in the air.

The SIBOR® technology makes it possible to take advantage of the excellent corrosion resistance of molybdenum both for large, complicated reinforcements which protect the tank from corrosion and also to protect molybdenum glass melting electrodes against oxidation while heating up the tank. Please see the PLANSEE technical information brochure “Glass Melting Electrodes” for more information on molybdenum glass melting electrodes and their protection with SIBOR®.

Unprotected throat at the end of a campaign



Molybdenum throat protection in a new glass tank

# Molybdenum throat protection

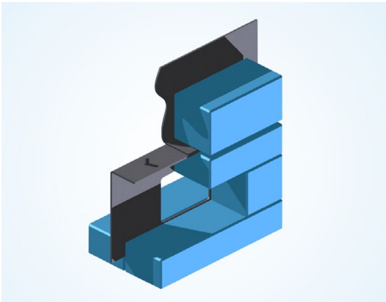
The throat is one of the most critical sections of the glass tank. It tends to be heavily eroded and corroded by the glass melt. The condition of the throat is of vital importance for the glass quality as well as for the length of a tank's service-life. A corroded throat often requires hot and sometimes even cold repairs. Reducing the need for such reconditioning in this critical area not only means making considerable direct savings on repairs themselves; it also ensures a stable and long-lasting high quality of the glass produced, as the dimensions of the throat have an impact on the rejection rates caused by knots or bubbles.

As previously mentioned, molybdenum has a much better corrosion-resistance against the glass melts than does the brick material. This difference actually increases with temperature; the higher the temperature the more favorable molybdenum is in comparison. The installation of molybdenum is thus especially recommended in high-melting and high-corrosive glasses like opal glass and borosilicate glass.

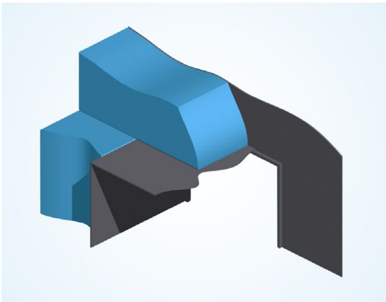
Some important design aspects have to be taken into consideration for glass tank reinforcements (GTR). All tolerances have to be selected to very tight limits and parameters, so as to ensure an exact fitting of the molybdenum parts. The gaps between the GTR and the neighboring bricks must be kept as small as possible in order to avoid local glass access.

In general the throat protection consists at least of the front plate assembly and the U-channel.

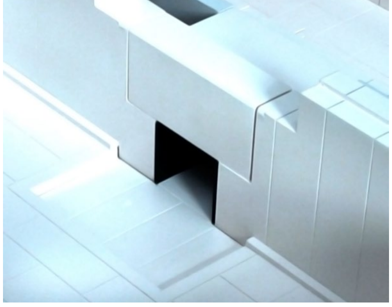
The size of the L-shaped front plate has to be large enough to cover the joint between the nearest bricks. For the purpose of firm and secure mounting, approximately 20 mm of the plate are clamped into the bottom bricks. Above, the short side of the front plate is fixed to the upper bricks. This assembly method inhibits any movement of the front plate in operation. For additional protection of the upper bricks the usage of a second L-shape protection is recommended.



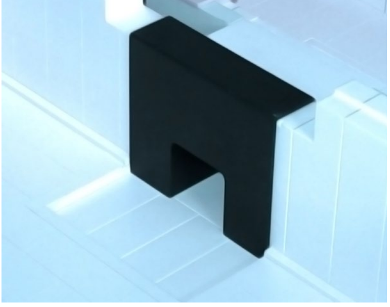
The U-channel is clamped directly onto the front plate by means of an inner profile. The profile is fixed onto the front plate, having exactly the same inner dimensions as the U-channel. This connection functions like a labyrinth, preventing any local glass penetration.



The U-channel is clamped into the floor bricks



The covering block is put on



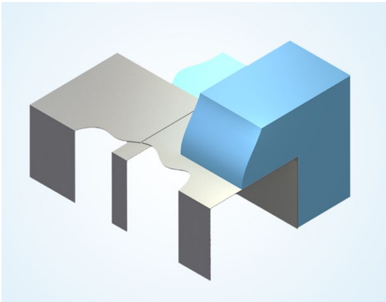
The front plate is pushed on

Fact Box

## *Installation of glass tank reinforcements.*

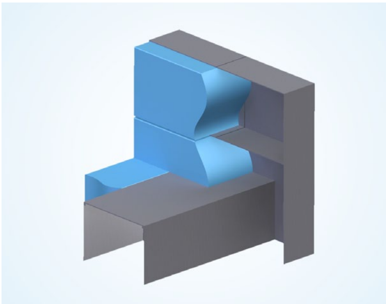
The glass tank reinforcement is designed as per customers' requests and to fit the specific furnace design. The tolerances for a precise fitting of the molybdenum parts and all connections are selected as tightly as possible. The integration of the GTR into the brick construction has to be closely discussed with the customer since some adaptions may be required.
In general the installation can be done by experienced furnace constructors during the rebuilding of the tank. At customer's request PLANSEE offers to procure reliable and experienced partner companies for the installation work.

The U-channel exactly covers the inner surface of the bricks along the throat. For convenient handling and installation the assembly is delivered in multiple parts, which can be easily connected during installation. Where U-channels longer than 600 mm are required, the protection can be extended as shown. An inner bracket holds the parts together, forming an even surface on the side facing the bricks, so that no additional machining is necessary. The bracket covers the gaps between the molybdenum parts to ensure that no glass melt can enter.

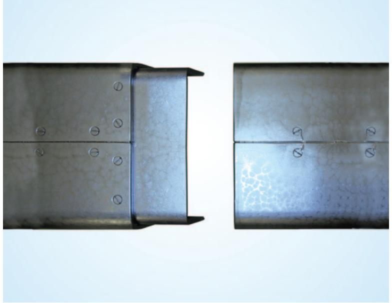


For high-corrosive glasses such as borosilicate or opal glass the so called "box-principle" for glass tank reinforcements can enhance the protection effect, by adding molybdenum flaps to the front plate.

Over the last five years, PLANSEE has successfully installed more than 50 GTR-projects.



Unprotected wall at the end of a campaign



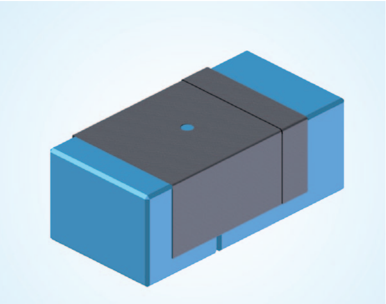
Detail of reinforcement design

# Protection of bubbler and crosswall

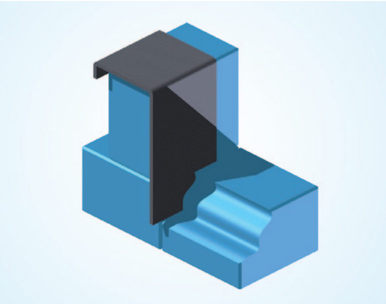
When planning a glass tank, special attention is given to the correct placement and sizing of the crosswall and, if applicable, the bubbler. These tank components are especially prone to heavy corrosion. And to make matters worse, corrosion problems with the bubbler and crosswall cannot be repaired hot, so that they exert a decisive influence on the length of service life. In many cases severe wear also occurs in the bottom area in front of the crosswall / bubbler, caused by the strong convective current.

Molybdenum reinforcements in these areas improve the tank durability. The dimensions remain unchanged for a significantly longer period and the functioning of the bubbler and wall is safeguarded, which is not the case with unprotected refractory bricks.

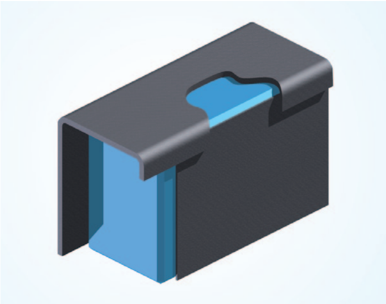
The design of the reinforcement consists of multi-part molybdenum profiles that fit over the bricks. The length of the individual parts is carefully chosen so that the plates cover the joints in the bricks of the crosswall or bubbler. The parts are assembled by means of a connection plate. There is no limit to the total length of such a reinforcement. Depending on the shape and size of the crosswall, the reinforcement can be designed to protect just the flow side or all sides.



Scheme of a bubbler protection in U-shape



Protection of wall in flow direction



Wall protection from both sides

Fact Box

All parts of the GTR systems are 100 % SIBOR®-coated to guarantee complete protection against oxidation.
The reinforcements are manufactured to the specified tolerances and checked both visually and by measuring during the final inspection. The thickness of the SIBOR® layer is carefully monitored.

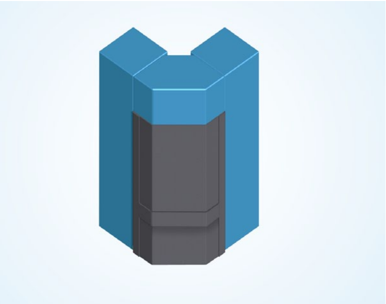
For the purpose of easy handling and installation, multi-part reinforcements are delivered disassembled with all required fixtures. Drilling templates to position the angled pins can be provided on demand.

Our experienced team is available for further questions and advice. Please contact your PLANSEE partner.

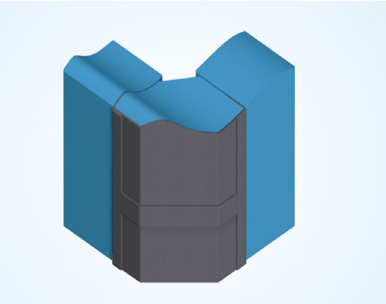
# Doghouse reinforcements

Another critically important area of a tank is the filling area – the doghouse. Strong abrasive corrosion is caused by the still partially solid filling material. Additionally the foam that develops at the 3-phase boundary chemically corrodes the AZS bricks. Lining the doghouse corners with SIBOR®-coated molybdenum plates reduces the attack significantly, as molybdenum withstands both the abrasive and the chemical pressures better than the refractory bricks.

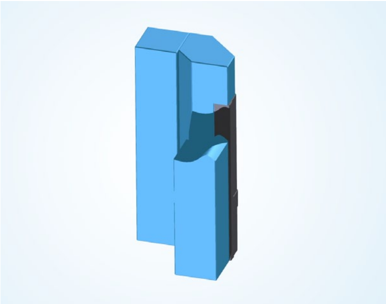
The reinforcements are tailored individually to customer requirements in terms of size and design. It is possible to construct one-piece and multi-piece variations that fit tightly. The reinforcements are secured with angled pins, which are set into the wall below the glass level. In addition the plates can be clamped into the floor bricks. This is a reliable way to protect the plates from tilting and falling over. The components have to completely cover all joints in the bricks. The upper edge of the reinforcement is dimensioned to match the minimum glass level. Eventually protruding molybdenum is sublimated by the oxygen in the air. Once this settling has taken place, the upper edge of the reinforcement remains stable despite normal variations in the glass level. In the area above the molybdenum plate the AZS bricks are still subjected to the attack of the 3-phase boundary. However, the molybdenum plate prevents an erosive current from forming and the corrosion of the bricks is reduced.



Doghouse protection overview



Clamping detail from front view



Clamping detail from side view

## Close to the customer - our global network

PLANSEE manufactures and markets its products worldwide. Production sites in Europe, USA and Japan and a global network of sales subsidiaries and sales partners, enable outstanding customer service and product quality delivered by local teams. Stronger than any alliance and more diversified than single producers, PLANSEE is the most reliable source for high performance components made of refractory metals.

For more information and local contacts please visit our website:

www.plansee.com

*A Step ahead in Technology.*

PLANSEE



7000998 - 719 TI EN 05.09 (1.500)