



School of Engineering

MSc Mechanical Engineering

M7X01385 - Mechanisms of Material Failure

Assignment - Significance and Properties of Coatings

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March 2019

Abstract

The report considers the application of a carbon steel glass lined chemical reactor vessel where corrosion of carbon steel in a sulphuric acid environment is detrimental to the vessel pressure shell. The improvements made through the application of a corrosion resistant borosilicate vitreous enamel coating and the method of application and adhesion in the interface are considered.

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1.0 Introduction

Sulphuric acid is widely used within the chemicals industry, being used to make many compounds which are utilised by manufacturing industries. The batch manufacture of compounds normally taking place within reactor vessels, which are either made of corrosion resistant materials or carbon steel incorporate a corrosion resistant containment lining. The report considers carbon steel reactor vessels utilising a borosilicate vitreous enamel coating acting as a containment lining to prevent corrosion of the carbon steel vessel substrate in the presence of sulphuric acid. The corrosion of carbon steel in the presence of sulphuric acid is discussed, also the application of a vitreous enamel coating to a steel substrate and the adhesion within the interface.

2.0 Glass Lined Reactors – Control of Corrosion by Vitreous Enamel Coating

2.1 Application of Glass Lined Reactors

Glass lined reactor vessels are specified in manufacturing processes where the process medium contains corrosive constituents that would compromise the vessel shell integrity due to corrosion, often occurring at an accelerated rate where elevated temperatures and pressures are present during the process. A typical reactor vessel being manufactured from pressure vessel grade low carbon steel, with a primary containment layer of borosilicate vitreous enamel built up of several layers on the inner containment surfaces. Other components associated with the supply and removal of the process medium in a typical reactor system are manufactured from borosilicate glass components, a typical reactor system is depicted in figure 1.

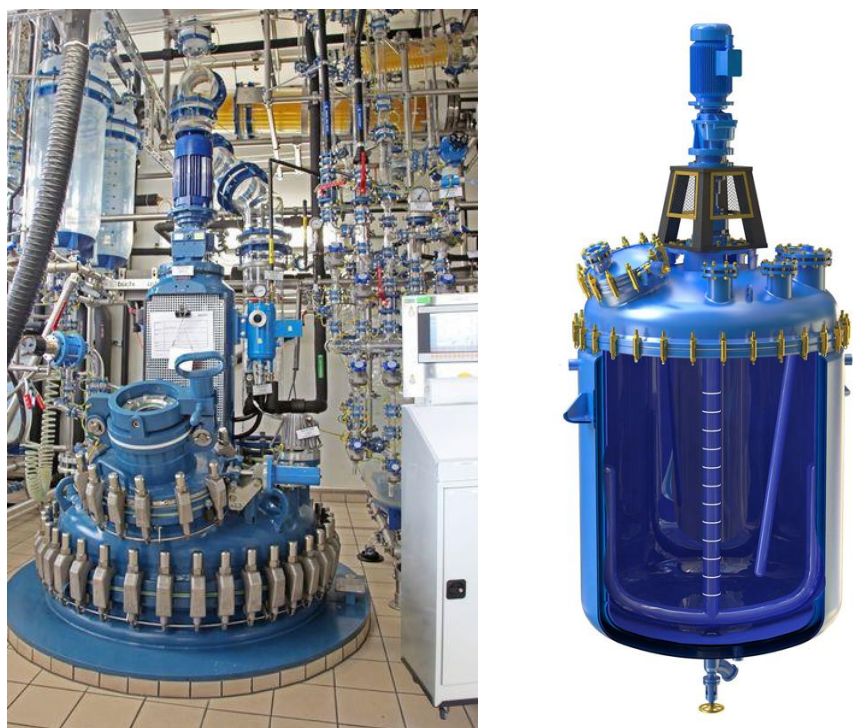


Fig 1. Reactor in situ (Buchiglasuster, 2019), Fig 2. Section view typical reactor (Pfaulder, 2019)

Reactor vessels are typically utilised industrially for the manufacture of wide range of chemicals where sulphuric acid is often specified as a constituent raw material of the production process, significant volumes of sulphuric acid are used in the production of organic chemicals (Speight, 2017). Batch type reactors (figures 1 & 2), are typically specified with volumes of between 10 and 1000 litres, with design pressures and temperatures in the range of $-1/+6$ bar and $-25/+200^{\circ}\text{C}$ respectively. Reactor design can also incorporate an external jacket to facilitate heating and cooling, and also agitation and mixing by glass coated mixers and stirrers (De Dietrich Process Systems, 2019).

2.2 Corrosion of Low Carbon Steel in a Sulphuric Acid Environment

Unprotected carbon steel in contact with sulphuric acid reacts to form iron sulphate and hydrogen (1).



The reaction is considered an aqueous corrosion mechanism where an electrolyte present conducts between anodic and cathodic areas present on the carbon steel surface, the respective anodic (2) and cathodic (3) reactions are described as follows



The iron sulphate forms a protective layer over the exposed carbon steel surfaces and prevents further corrosion. However, the iron sulphate layer is easily disturbed by turbulent fluid flows (Louie, 2010), resulting in further corrosion. Whilst it is possible to store concentrated sulphuric acid in carbon steel tanks where the disturbance to the sulphate layer is minimal, accelerated corrosion is inevitable in a reactor vessel due to the turbulent nature of the mixing process and possibility of inclusion of abrasive constituent parts of the process medium. The iron sulphate is also soluble in sulphuric acid, the rate of which is dependent on the concentration, where the concentration of the acid is greater than 90% the solubility of iron sulphate decreases (Dean & Grab, 1986).

The rate of corrosion is also dependant on temperature, for static conditions the rate of corrosion in carbon steel tanks containing sulphuric acid at a concentration of 98% is approximately 10 times greater at 107°C, 5mm/y, when compared to 24°C, 0.5mm/y (NACE, 2006) as described in figure 3.

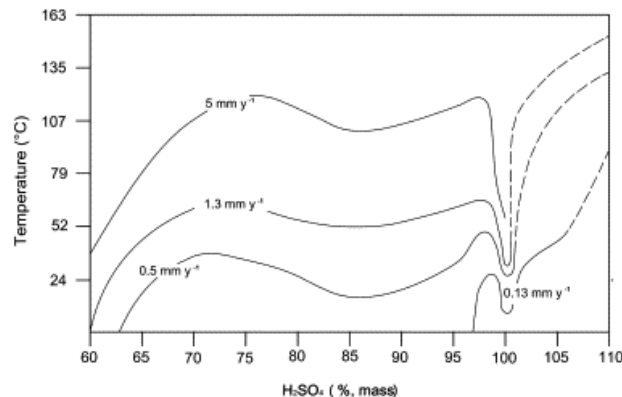


Fig 3. Temperature and sulphuric acid concentration effect on rate of corrosion (NACE, 2006)

2.3 Corrosion Resistance of Vitreous Enamel in a Sulphuric Acid Environment

A borosilicate vitreous enamel layer applied to the inner surface of the reactor vessel acts as an effective corrosion protection layer (Wu, et al., 2010) which significantly increases the service life of the vessel protecting the carbon steel substrate from corrosion by direct contact with sulphuric acid. Comparison of manufactures data describing wear rates for vitreous enamel where sulphuric acid is present against unprotect carbon steel shows a considerable improvement in resistance to acid corrosion. The graphical representation in figure 4 describes the corrosion rate of a proprietary grade of vitreous enamel 'DD 3009 glass' manufactured by De Dietrich Process Systems which finds application as a reactor coating material.

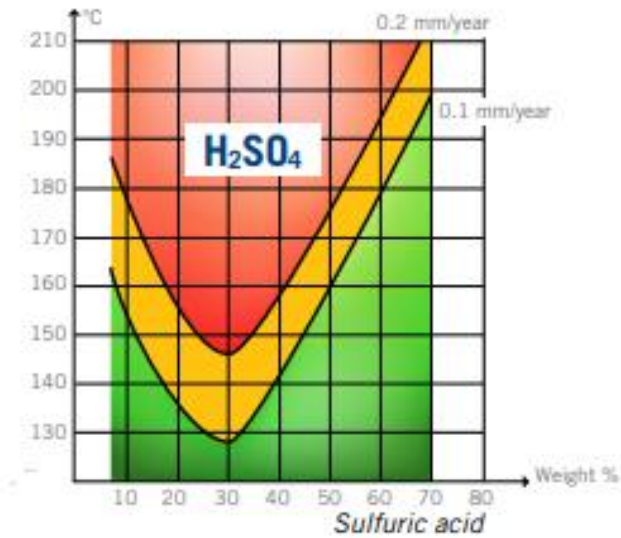


Fig 4. Temperature and sulphuric acid concentration effect on rate of wear to DD 3009 glass (De Dietrich Process Systems, 2019)

Comparison of figures 3 and 4 where sulphuric acid is between 60-70% concentration demonstrates the considerable corrosion resistance properties of borosilicate vitreous enamel over carbon steel, where the steel corrodes at a rate 50 times greater at a temperature 107°C when compared to the borosilicate vitreous enamel at 180°C.

The borosilicate vitreous enamel coating utilised within reactors not only provides excellent resistance to sulphuric acid, but also most other acids and alkalis, with the notable exceptions of hydrofluoric and hot concentrated phosphoric acid (De Dietrich Process Systems, 2019), the application of borosilicate vitreous enamel coatings enables the broadest range of corrosion resistance when compared to other corrosion resistant materials applied as reactor lining as described for DD 3009 glass produced by De Dietrich Process Systems in figure 5.

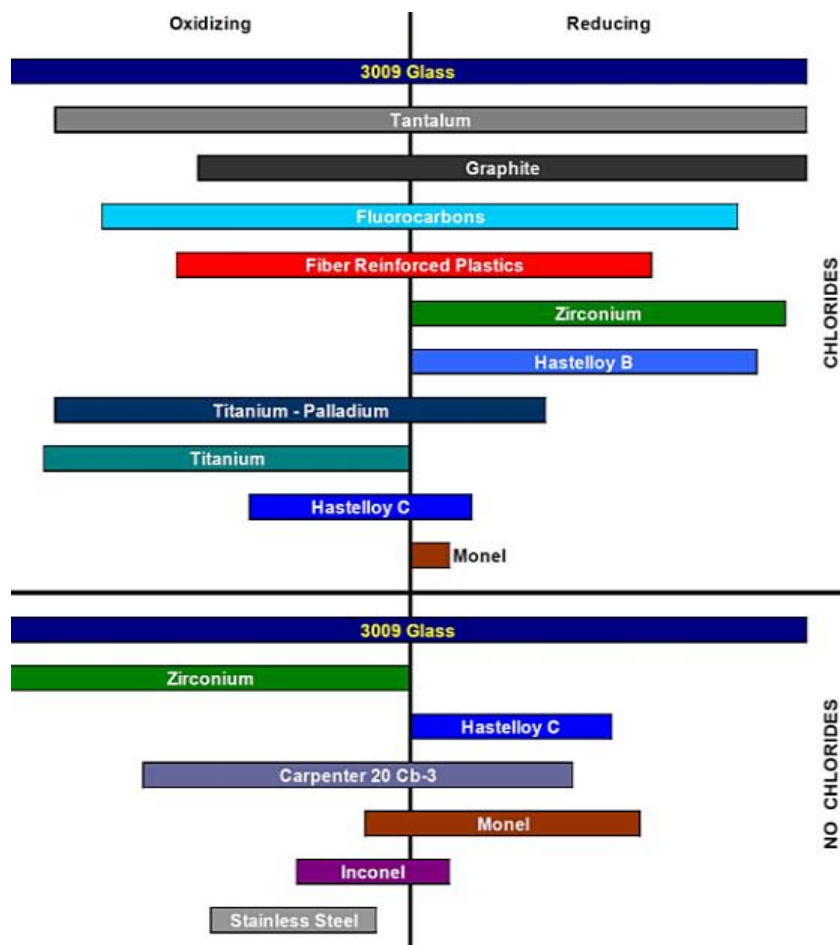


Fig 5. DD 3009 glass corrosion resistance compared to other common corrosion resistant materials. (De Dietrich Process Systems, 2019)

Other notable properties of borosilicate vitreous enamel coatings applied to reactor vessels in addition to corrosion resistance.

- Surface finish – Smooth surface which has excellent scratch resistance, also reduced amount of product fouling and ease of cleaning between processes (Surface Technology, 2019).
- Contamination – Due to the low rate of wear 0.1mm/year, contamination of the process fluid is often negligible when compared to other lining materials or the vessel substrate. Finds application in high purity processes such as pharmaceuticals. No catalytic effect which could potentially occur with exotic metals (Glascoat, 2019)
- Cost efficiency – Utilising a relatively inexpensive low carbon steel substrate and applying a vitreous enamel coating has a significant reduction in capital cost over the specification of more exotic metals described in figure 5. A reactor can also be 're-glassed' when the lining has worn to unacceptable limits, which could result in a significant cost saving when compared to a new vessel and also the associated reduction in delivery time (Pfaulder, 2019).

3.0 Coating – Vitreous Enamel on Low Carbon Steel Substrate

3.1 Vessel Design

The design of carbon steel pressure shells which are subject to vitreous enamel coating differs from vessels which are unlined or are coated with polymers or hot dip zinc, as fillet joints and fillet welds are avoided, all nozzles on the shell and heads of the vessels are formed by a swaging process to minimise stress concentration within the coating and to aid cleaning when in service (De Dietrich Process Systems, 2019).

3.2 Vessel Surface Preparation

To achieve a satisfactory coating the surface preparation of the substrate is critical in ensuring sufficient adhesion and surface appearance is achieved.

As the pressure vessel shell is formed from hot rolled steel the initial surface preparation process involves shot blasting, this removes mill scale from the surface of the steel also increasing the surface roughness and contact surface area in the same process.

On completion of shot blasting the vessel is degreased in an alkaline degreasing bath, followed by rinsing in a water bath. The final step consists of pickling in a sulphuric acid bath and further rinsing in a water bath, the pickling increasing the surface microroughness with focus on the grain boundaries (ArcelorMittal, 2019).

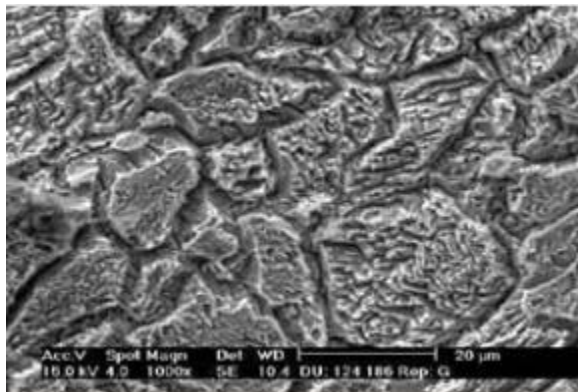


Fig 6. Ideal surface pickling (ArcelorMittal, 2019)

3.3 Vitreous Enamel Preparation

The enamel mixture dependant on properties required is mixed and melted within a furnace, then poured as a liquid into a water bath where the sudden cooling fractures the enamel into smaller particles referred to as 'frit'. Further processing involves grinding the frit into a powder for application to the substrate.

3.4 Coating Substrate with Vitreous Enamel

The borosilicate vitreous enamel coating is made up of several layers which on completion typically result in an overall coating thickness of 1-2mm. The first coating applied is referred to as the ground coat, this typically has properties which aid adherence to the steel substrate, with cobalt oxide being a common adhesion additive. The carbon content of enamelling steels is typically in the range of 0.02% to 0.10%, however typical pressure vessel grade steels generally have a higher carbon content with P275NH and A515 Grade 55(380) typically being 0.16% and 0.18% respectively. The higher carbon content placing importance in establish the correct properties of the ground coat to ensure suitable adherence to the substrate. The ground coat may well have poor corrosion resistance; however, the subsequent cover coats have properties specifically aimed at corrosion resistance. Figure 7 details the ground coat and cover coat applied to the substrate.

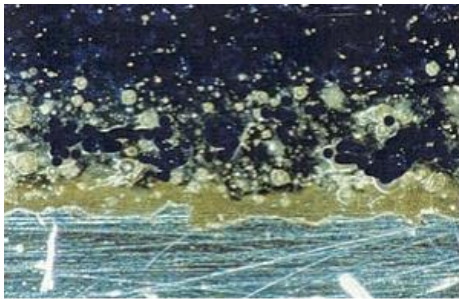


Fig 7. Image of cover coat, ground coat and substrate bonding (De Dietrich Process Systems, 2019)

The vitreous enamel ground and top coats are applied by a manual spray technique to the inner surface of the vessel one coat at a time, the coating allowed to dry before firing. The skill and experience of the operator being an important consideration in coating thickness control.



Fig 8. Manual spray application of enamel coat (The Vitreous Enamellers Society, 2019)

Fusing the enamel to the steel substrate takes place within a temperature controlled electric furnace, where the specified firing temperature and soak time are closely controlled, temperatures for steels being in the range of 780 - 850°C. The vessel being removed and allowed to cool under controlled conditions before inspection and application of subsequent cover coats which are each subject to the same heating, cooling and inspection process, albeit at reducing temperature to control the mixing of proceeding layers.

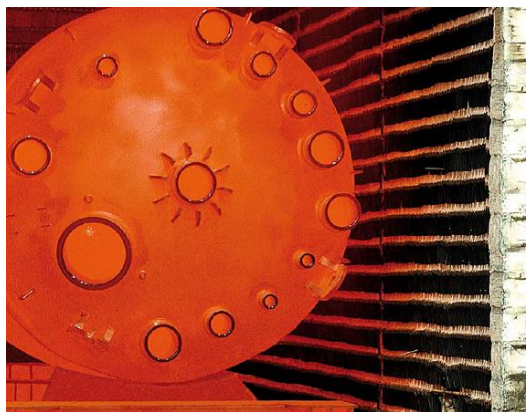


Fig 9. Vessel on completion of firing cycle (De Dietrich Process Systems, 2019)

3.5 Inspection and Testing

The inspection of the glass lining takes the form of visual inspection and also thickness and integrity testing, such tests are carried out during manufacture between enamel coats and on final approval and also during the service life of the reactor vessel. Inservice inspection being an important tool in assessing the remaining service life of the reactor vessel before re-glassing is required and identifying smaller local defects that could lead to product contamination and rapid corrosion of the steel substrate if left untreated, such small defects are repaired by inserting a tantalum plug in most cases.

To establish the thickness of the vitreous enamel lining a magnetic thickness coating gauge is utilised where the substrate is a magnetic steel, and eddy current testing where a non-magnetic stainless steel is specified (BINDT, 2019). To establish the integrity of the vitreous enamel coating a spark or holiday test is utilised. The equipment applies a voltage which can run into several thousands of volts depending on the thickness of the coating, from an insulated metallic brush across the vitreous enamel surface, the steel substrate being grounded. Any defects such as pinholes or other discontinuities result in a spark being produced as the voltage travels to the grounded substrate, allowing identification of the defective area of the coating. (ASTM, 2015).

4.0 Vitreous Enamel – Steel Substrate Interface

The adherence of the borosilicate vitreous enamel ground coat to the steel substrate at a microstructure level is of significant importance in ensuring a satisfactory bond between the two materials is achieved.

The thermal expansion coefficients of both materials must be considered, with the vitreous enamel being specified to ensure that it remains in compression on cooling, due to ceramics being weak in tension. The amount of silica present within both the ground coat and top coat was shown to affect the tension between the vitreous enamel and the steel substrate (Reis, et al., 2019), where an increase in silica 10% above the desired composition to ensure acceptable thermal expansion resulted in poor adhesion. Where adhesion is assessed by impacted testing conducted in accordance with ISO 4532 Vitreous and porcelain enamels – Determination of the resistance of enamelled articles to impact – pistol test.

The adherence mechanism is described in two main theories, being mechanical and chemical oxide. Earlier work and literature review by Sturgeon (1987), suggests that a roughened substrate contributes to the adhesion but is not the principle mechanism, rather the adherence is developed by the chemical bond and solubility of the substrate oxide layer in the vitreous enamel ground coat. However later analysis of the adherence within the interface by Shieu, et al. (1999), argue that mechanical interlocking is the controlling mechanism, where high density anchor points are identified. Cobalt was identified as a constituent within the ground coat frit which influenced the development of anchor point on the substrate surface.

The presence and effect of cobalt as a constituent within the ground coat frit is further confirmed as promoting adhesion by dendritic and chemical theories in separate studies completed by Samiee, et al. (2007) and Isiksacan, et al. (2015), the dendritic formations within the vitreous enamel and substrate interface are identified as oxidation of the substrate material.

A study completed by Bodaghi & Davarpanah (2011) found that the cobalt content of the ground coat frit affected the formation of dendrite in that an increase in cobalt increases the interface while reducing the size. Cobalt was also credited with reducing fish scaling defects within the interface. Bodaghi & Davarpanah (2011) further argue that cobalt influences galvanic corrosion which is associated with promoting adherence.

The addition of cobalt to the ground coat frit influences the adherence within the interface of the vitreous enamel and steel substrate both chemically and mechanically and would suggest that both mechanisms contribute to adherence. The interface is described within figure 10 and 11, containing micrographs of an enamel-steel substrate interface containing no cobalt (a), and cobalt (c). The ferrous-cobalt alloy can be seen to increase surface area by the development of anchor points.

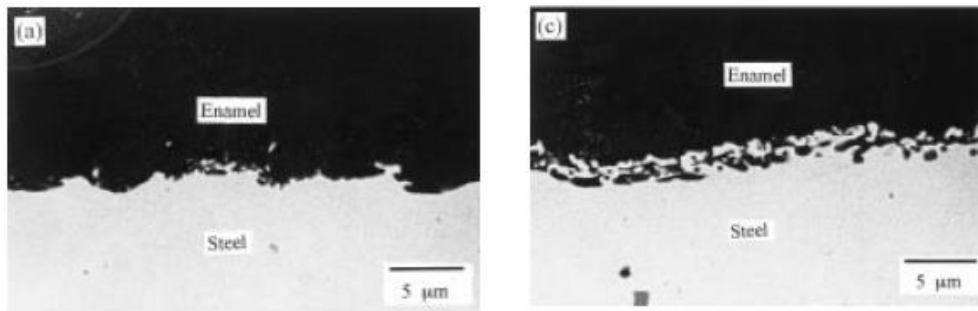


Fig 10 & 11. SEM micrographs (adapted from Shieu, et al., 1999)

The addition of nickel oxide to the ground coat frit composition was also noted of importance in the development of steel substrate surface roughness (Hossain, et al., 2014). With a nickel oxide content of 0.5% of the composition being normal for enamelling grade carbon steels. Further research into a patent registered by the A. O. Smith Corporation (1999), detailed the addition of nickel oxide in the range of 2 to 10% composition of ground coat where the application was concerning carbon steel substrates with a carbon content between 0.1 to 0.3%, aligning with hot rolled low carbon steels used in pressure vessel manufacturing.

5.0 Conclusion

Whilst low carbon steel is relatively well protected against further sulphuric acid corrosion due to the iron sulphate layer formed, it is easily removed by agitation. The specification of low carbon steel would be acceptable within storage tanks where the velocity and turbulence of fluid would cause minimal disruption, however unprotected chemical reactor vessels would be subject to an unacceptable rate of corrosion. The introduction of a borosilicate vitreous enamel barrier coating provides acceptable levels of wear resistance against process mediums and sulphuric acid encountered within chemical reactor vessels. The borosilicate vitreous enamel coating also has additional benefits of being easily cleaned, highly scratch resistant and introducing negligible contamination to the process fluid. Significant cost savings can be achieved by using glass lined vessels as they are easily re-lined when the coating has reached its design service life. The composition of the ground coat, and notably the inclusion of cobalt and nickel oxide has a significant influence on the adherence of the vitreous enamel to the low carbon steel substrate at the interface.

6.0 References

ArcelorMittal, 2019. *Steel for enamelling*. [Online]

Available at:

https://constructalia.arcelormittal.com/files/A103_Steelforenamelling_usermanual_EN_pdf3--7d70d8cc257b1d95905bed6c02743fa5.pdf

[Accessed 20 April 2019].

ASTM, 2015. *ASTM D5162-15 Standard Practice for Discontinuity (Holiday) Testing of Nonconductive Protective Coating on Metallic Substrates*. s.l.:ASTM.

BINDT, 2019. *Coating thickness measurement methods*. [Online]

Available at: <https://www.bindt.org/What-is-NDT/Coating-thickness-measurement-methods/>

[Accessed 23 April 2019].

Bodaghi, M. & Davarpanah, A., 2011. The influence of cobalt on the microstructure and adherence characteristics of enamel on steel sheet. *Processing and Application of Ceramics*, 4(5), pp. 215-222.

De Dietrich Process Systems, 2019. *Chemical Reactors*. [Online]

Available at: <https://www.ddpsinc.com/de-dietrich-expertise/reactors>

[Accessed 4th March 2019].

Dean, S. W. & Grab, G. D., 1985. Corrosion of carbon steel by concentrated sulfuric acid. *Materials Performance*, 24(6), pp. 21-25.

Dean, S. W. & Grab, G. D., 1986. Corrosion of carbon steel tanks in concentrated sulphuric acid service. *Materials Performance*, 25(7), pp. 48-52.

Glascoat, 2019. *Technical specifications*. [Online]

Available at: <http://glascoat.com/webfiles/file/8.pdf>

[Accessed 07 May 2019].

Hossain, A., Ahmed, A. N. & Khan, A. A., 2014. Vitreous Enamel Coating on Mild Steel Substrate: Characterization and Evaluation. *International Journal of Scientific & Engineering Research*, 5(2), pp. 821-826.

International Organisation for Standardization, 1991. *ISO 4532:1991 Vitreous and porcelain enamels - Determination of the resistance of enamelled articles to impact - Pistol test*. Geneva: International Organisation for Standardization.

Isiksacan, O., Yesilcubuk, A. & Yucel, O., 2015. Substrate-Enamel Interface relation and Impact on Quality of Enamel. *The Minerals, Metals & Materials Society*, Volume 144, pp. 1523-1530.

Louie, D. K., 2010. *Handbook of sulphuric acid manufacturing*. 2nd ed. Ontario: Richmond hill.

NACE, 2006. *SP0294-2006: Standard practice – Design, fabrication, and inspection of storage tank systems for concentrated fresh and process sulfuric acid and oleum at ambient temperatures..* Houston: National Association of Corrosion Engineers.

Pfaudler, 2019. *Reconditioning and Reglass*. [Online]
Available at: <https://www.pfaudler.com/en/products/recondition-reglass#lightbox>
[Accessed 07 May 2019].

Reis, S. T. et al., 2019. The Effects of Silica on the Properties of Vitreous Enamels. *Materials*, 12(2), p. 248.

Samiee, L., Sarpoolaky, H. & Mirhabibi, A., 2007. Microstructure and adherence of cobalt containing and cobalt free enamels to low carbon steel. *Materials Science and Engineering*, A(458), pp. 88-95.

Shieu, F.-S., Lin, K.-C. & Wong, J.-C., 1999. Microstructure and adherence of porcelain enamel to low carbon steel. *Ceramics International*, 25(1), pp. 27-34.

Speight, J. G., 2017. *Environmental Inorganic Chemistry for Engineers*. 1st ed. Cambridge, United States: Butterworth-Heinemann.

Sturgeon, A. J., 1987. *University of Warwick Publications service & WRAP - Glass-ceramic coatings for metals*. [Online]
Available at: <http://wrap.warwick.ac.uk/34630/>
[Accessed 25 April 2019].

Surface Technology, 2019. *Enamelling*. [Online]
Available at: <http://www.uk-finishing.org.uk/N-COAT70/enamelling.htm>
[Accessed 07 May 2019].

The Vitreous Enamellers Society, 2019. *Vitreous Enamel - Industrial*. [Online]
Available at: <https://www.iom3.org/vitreous-enamellers-society/vitreous-enamel-industrial>
[Accessed 15 April 2019].

Wu, P. P. et al., 2010. Corrosion Behaviors of Borosilicate Glasses in Various Leaching Agents. *Advanced Materials Research*, Volume 177, pp. 466-469.