Maintenance as instrument to ensure the operation in sulphuric acid plants

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In spite of careful and ever more refined processing at plants, and the further developments constantly being made in corrosion protection materials, regular downtimes are inevitable due to the aggressive operating conditions prevailing at such facilities, particularly at sulphuric acid plants. The full gamut of corrosion protection work is carried out during such downtimes, beginning with repairs to floors and ditches, continuing on to partial replacement of parts of the masonry in absorption towers, heat exchangers and pump-tanks, and on down to the switching out of complete components of the plant.

This kind of work is made more difficult by the extremely narrow window of time available due to reasons of production capacity, but also due to the amounts of concentrated sulphuric acid always extant in all parts of the plant, something that requires comprehensive occupational safety measures to be taken. Because masonry materials are virtually saturated with sulphuric acid after a certain time in operation, conditions similar to a stalactite cave have to be expected for all parts within the plant components concerned. This means that such work, e.g. within an absorption tower, is only possible with acid resistant rubber suits and external breathing apparatus. Due to the enormous physical strain this causes for workers, such work has to be carefully planned in terms of scope, available time and the staffing capacities involved.

From a technical point of view, the work necessary to connect new pieces of masonry to existing linings turns out to be very difficult because the surface is contaminated with sulphuric acid. The aging processes induced by the sulphuric acid, e.g. those encountered on a polyisobutylene sealing strip in a drying tower, create difficulties when connecting the old liner up to the new.

This presentation is intended to depict the problems faced when sensibly and purposefully maintaining and servicing a sulphuric acid plant. It will go through the necessary repairs without losing sight of the requirements for available production capacities.

In terms of process technology, sulphuric acid is primarily generated nowadays using the contact method in which the required sulphur dioxide (SO_2) is produced at a roasting facility in a fluid bed roasting furnace or by combusting sulphur in a sulphur combustion furnace. Due to the reaction temperatures of 1200°C – 1600°C the process requires, these facilities have to be protected with a refractory masonry lining. Damage occurring in this area during operation is thus, naturally enough, mainly caused by temperature. For instance, if the oxygen content during combustion of the sulphur is too high, this can cause an increase in combustion temperatures, which can in turn result, under extreme conditions, in a failure of the carefully constructed and finely tuned corrosion protection system. Because the heat insulation is now no longer sufficient, temperature break-outs into the steel and/or sintering processes within the masonry can occur. These can then be observed in changes in the technical properties of the lining which, in the medium term, can make a replacement of the lining or even the entire facility, including the steel, unavoidable.

The period of time that elapses until this occurs depends, however, strongly on the materials used and how well and properly they have been installed. Because the mechanism by which damage occurs, as described above, is not unknown, it is recommended that both the lining thickness and the materials used for the lining be adjusted to take account of this situation. In other, clearer words: This requires a selection of high-quality products, on the one hand, and an increase in lining thickness on the other.

In the further course of sulphuric acid production, SO_2 gases from roasting or sulphuric combustion enter a Venturi scrubber where they are cooled and cleaned. Seen in terms of corrosion technology, the Venturi head with its gas outlet and the nozzle ceiling represent the problematic zone here.

The chemical protection required for the steel structure is usually offered by a rubber lining membrane that is created either as an in-plant prefabricated membrane or as one applied on-site. To protect the rubber lining from too extreme temperatures (after all, the gases in the outlet have temperatures around 400°C), appropriate protection in the form of masonry has to be applied. Plans will call for an insulating ply of foam glass as a first layer over the rubber lining, the result of a heat penetration calculation that will have to take account of the interior temperatures actually occurring along with such ambient values as exterior temperature, solar radiation and wind speed. The further structure of the plies can then be made up of one of light refractory brick and, as contact layer with the media, one of acid-resistant ceramic brick, jointed with potassium silica cement. The nozzle ceiling also has to be lined with these temperature-reducing plies. As an inner ply facing the media, however, a variety of different brick grades have to be used depending on the temperature as, particularly in this zone, high loads are incurred by temperature fluctuations (hot/damp) that the structure chosen has to withstand. At temperatures in a range up to 400°C, graphite brick is used here, at higher temperatures highly refractory grades. In the damp area, i.e. the impact area of the cone, the lining will have at least two plies. The first ply consists of acid-resistant ceramic brick and the second, if required – for fluoride conditions – of carbon brick. The lower cone and the lower box usually receive a single ply of masonry for cost reasons, depending on the load there either of acid-resistant ceramic brick or with carbon brick.

In spite of a careful selection of the materials or material combinations to be used, the cement joints in the upper part of the Venturi are often washed out, a commonly observed pattern of damage. Hot gas entering the Venturi with 350 – 400°C has to be properly cooled. The actual gas entry point is only exposed to a dry load and can be lined in the conventional manner of acid-resistant brick bedded and jointed in potassium silica cement. The Venturi ceiling connected to the gas inlet requires more complicated technical solutions on the side in contact with the media. In spite of their excellent resistance to acid, even at high temperatures, conventional potassium silica cements only display moderate to poor resistance to washing out. A switch to a potassium cement optimised particularly for resistance to washing out is thus imperative. The maximum temperature resistance of potassium silica cements presently available with the properties so described is approx. 450°C and thus still about 50K above the typical temperatures of gas entering this type of equipment. It does not become problematic until a high temperature meets hydrofluoric acid, a combination typical for steelworks. Due to the poor chemical resistance of cements containing SiO_2 (these include potassium silica cements), only SiO_2 free cement materials can be used in those kinds of conditions. This limitation leads compulsorily to a resin-bonded system based on furane resins. However, for all the advantages in terms of resistance to washing off and chemical attack, the problem encountered with this alternative is actually the temperature resistance values. At 300 °C short-term peak resistance and a value of around 230°C for long-term resistance, all the resin-bonded systems currently on the market have reached their limits. Due to these limits to resistance, the joints in these areas have to be reworked at regular intervals. As a rule, these temperatures initially cause a kind of coking of organic material in the cement joints. The carbon-rich layer building up here serves, for a certain time, as a protective layer, but will then later be washed out of the joint. If servicing intervals are maintained and the joints are repaired regularly, experience over recent years has shown that, in spite of weakness in terms of temperature resistance, the long-term stability and with it the operational safety of these alternatives, even in hydrofluoric acid loads, is preferable over time to the alternative offered by potassium silica cement.

The still damp SO_2 gas leaving the Venturi scrubber is dried by coursing through a damp electric filter in a drying tower together with concentrated sulphuric acid and then led into a contact boiler. In principle, both the drying tower and the interim and end absorbers are very similar in their operational conditions. In all those cases, the conditions are caused by concentrated sulphuric acid (drying tower 93 – 98%, absorber 95 – 98 %). Unalloyed steel (C steel) is resistant to sulphuric acid concentrations over 92 - 93% H_2SO_4 to a maximum of 25°C. The reason for this resistance lies in the formation of a thin layer of iron (II) sulphate that is, however, dissolved at higher temperatures and thus loses its protective effect. C steel is not resistant over the long term to streaming sulphuric acid either, as the thin passive layer is constantly being washed off. On the other hand, if a 2 mm thick ply of polyisobutylene liner is adhered to the steel surface and protected with masonry made of acid-resistant brick and suitable bedding materials, the result is a material composite that is virtually unlimitedly resistant to hot, concentrated sulphuric acid and attacks to the material from streaming abrasion. The decisive points for durability are the type of lining materials used and above all the absolutely correct manner the masonry work is installed.

Damage to the masonry can enable hot, streaming, concentrated sulphuric acid to gain direct access to the polyisobutylene liner. In such cases, first the carbon-rich surface layer building up on the liner is worn down constantly by the current, and this continues until the acid reaches the steel substrate. The effect of the formation of this protective layer on the liner, which is due to unavoidable small contact points with the concentrated sulphuric acid through capillaries and micro-tears in the masonry, can only remain permanent if this layer is not washed away. This is only the case if the masonry is intact and free of tears.

As a rule, therefore, the area beneath the cantilevered domed latticework is provided with three layers of masonry, with two layers above the latticework around the packed bed and a single layer further above this (40 or 65 mm). This is, however, only a general guideline. In practice, the thickness of the masonry and the number of brick layers can and does vary, dependent particularly on the size of the tower as well. To avoid damage to the masonry as far as possible and, together with it, downtimes with the loss in production they incur, Finite Element Analyses are carried out in the planning and construction phase to obtain details on the areas under particular threat at the transition points to fittings onto the coated masonry, such as acid muffs or gas inlets, and on the procedures required to install a corrosion protection system. This type of lining using a membrane is standard, at least for drying towers: on the other hand, interim and end absorbers are often provided with only one layer of masonry. In this case, a ply of potassium silica cement is trowel-applied to the blank sandblasted steel plate or adhered to the steel substrate with ceramic paper saturated in soluble potassium. The preliminary masonry is then applied, made of acid-resistant ceramic brick, bedded and jointed in potassium silica cement. Because the adherence of potassium silica cement to steel is relatively poor, a gap can appear between the lining and the steel plate in which a thin film of concentrated sulphuric acid unavoidably gathers in the course of time. Then there forms first a very thin layer of iron (II) sulphate crystals on the steel plate, but this has a rather more passive effect, a protective effect which is lost at higher temperatures, however, because the iron sulphate then goes into the solution. Such layers of iron sulphate can grow considerably over time and create such tension in the masonry that a larger portion of the brick lining can break apart during repair work. Unfortunately, such phenomena often do not become apparent until repair or demolition begins, which in turn means that very rapid decisions have to be made on further steps to be taken in the process. Depending on the location of the damaged area, it is sometimes completely impossible to break out large areas as otherwise the structure and stability of the remaining masonry would be compromised! Here, the iron sulphate will remain on the steel casing as a passive layer. If any new ingress of hot concentrated sulphuric acid is prevented, the protective function of this layer will remain intact.

Regardless of the corrosion protection system used, it is inevitable that, after a certain time in operation, parts of the facility, such as the gas inlet in the drying towers or quenching towers, or even whole sections of the facility, will have to be replaced. The replacement of a gas inlet muff, which experience shows has yet to suffer damage, is, in technical terms, unproblematic. After removal of the old lining in the transitional area from muff to tank, the old muff is separated and lifted out of the plant. The new muff is then lifted in, positioned exactly and welded in properly. After the required pre-treatment of the steel substrate by means of sandblasting, the new lining of this portion of the surface is easy to do. Problems only exist similar to those already described for the transitional area between old and new corrosion protection system. To save time and thus prevent losses in production, there is, for instance, an opportunity to prefabricate as far as possible the membrane being planned for that area (rubber lining, polyisobutylene liner) so that only the contact points between old and new lining system have to be made on site. If partial repair is no longer possible, complete replacement of the entire facility will be the only possible option. When complete replacement is required, absorption towers and sulphur combustion furnaces pose, naturally enough, a challenge due to their size, specifically in terms of the downtimes required and actually available. For several years, such a facility is thus provided with masonry up to a certain point (e.g. half the height of the drying tower including free-standing domed latticework) next to the existing facility (that is still in operation) and is then lifted into its final position in this condition with a heavy crane. Not until this point in time does the actual downtime at the plant begin. This is a way to drastically shorten both downtimes and with them losses in production. In general, it must be stated concerning all facilities in plants of this kind that many problems cannot be found until the plant is switched off. Damage to the flange connections, for example, can naturally only be discovered after these have been unscrewed. During such downtimes, it is thus essential that all assembly personnel working on the site react rapidly to and have experience with such downtimes, and this means on the part of all companies involved in the work who have based their calculations on material and staff plans that have been done with proper foresight.

Another important area to be protected is, of course, floors, trenches and channels in such a plant. The load here is sometimes also due to dilute acids, also only for brief periods, and is thus much lower than in the actual plant and facility itself. Traditionally, protection here is provided through such liquid-tight coatings as those on an epoxy resin or polyurethane base which are then covered over with a ceramic tile bedded and jointed in phenol or furane resin or also potassium silica cement. Gutters and channels are protected over the long term using the thermoplastic materials described above.

Summary

For decades now, a wide variety of materials have been used successfully in corrosion protection. The product range here encompasses liners, linings using rubber or thermoplastic sheeting and combined systems. The extensive range of materials on offer allows installers to cover all sorts of loads and conditions in plants where sulphuric acid in produced and used. However, if it comes to failure of the lining after longer operational periods, further developments in application technologies and in the materials themselves have made it possible to repair such damage properly and appropriately even in very brief downtimes. Due to the appropriate norms and quality-assurance steps taken during production, application and finishing of corrosion protection systems, a consistently high quality standard can now be assured. Only through this interplay of engineering, top-quality products and careful installation by highly qualified expert personnel can production capacities be properly planned over the long term.