The use of carbon fiber reinforced DIABON® graphite tubes in shell and tube phosphoric acid evaporators

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Abstract:

For numerous decades, resin impregnated graphite has been the material of choice for the construction of phosphoric acid evaporators. The material has an outstanding resistance to every type of green phosphoric acid produced in the world and this independent of their fluoride and chloride content. When totally graphitised, the material also posts an outstanding thermal conductivity of approximately 80 W/m.K.. Which makes it a suitable material for the manufacturing of heat exchangers. Unfortunately, the material also has a reputation in the phosphoric acid industry for its sensitivity to mechanical and thermal shocks as well as its limited resistance to erosion.

SGL Group has developed in the early 1990’s a carbon fiber reinforced graphite tube that substantially alleviates the previously described inconveniences while maintaining the performance characteristics of the material and bringing operational reliability to the green phosphoric acid evaporation process. The first installed evaporators with carbon fiber reinforcement have been now in operation for more than 20 years. This gives us a clear picture of the real benefits of this technology and helps to suggest additional measures to progress further towards operational excellence.

The results of the tests originally carried out in our laboratories when we developed the carbon fiber reinforced tubes have been confirmed by the experiences accumulated by all of our customers around the world. It shows a significant improvement of the tubes mechanical properties resulting in a substantial reduction in the number of broken tubes. Commonly, a reduction by a factor of 20 times has been commonly observed in the number of tubes broken in operation, thus resulting in an extension of the equipment lifetime.

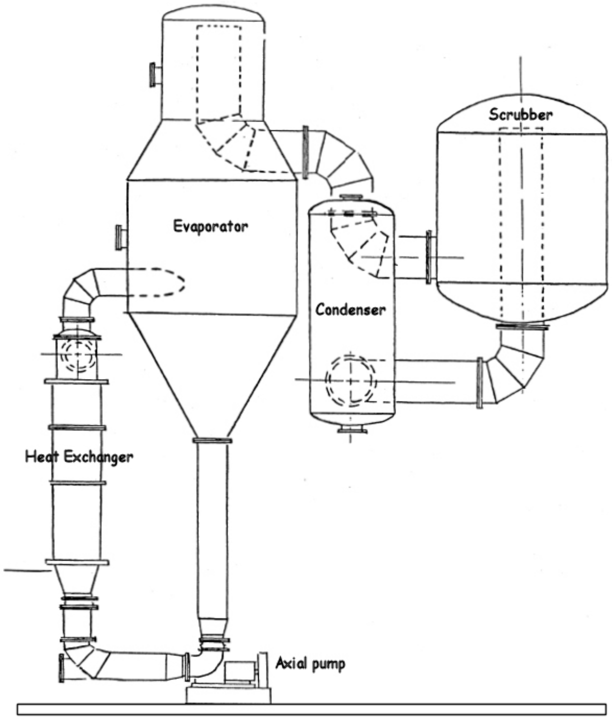
These years of operation also suggests that the use of a chemical cleaning method instead of water blasting improves even further the equipment reliability. In addition, it suggests that the proper design of steam and condensate lines is another key to operational reliability and equipment lifetime.

1. Process and Process Conditions:

The different wet phosphoric acid processes produce green acids with concentrations between 28 and 30 % P_2O_5 for the conventional dihydrates (DH) process either with a single or multiple reaction tanks, between 30 and 32 % P_2O_5 for the hemihydrates recrystallization (HRC), between 32 and 36 % P_2O_5 for the dihemihydrates (DHHH), between 40 and 42 % P_2O_5 for the hemihydrates (HH) and between 40 and 54 % P_2O_5 for the hemidihydrates (HDH).

For many technical (precipitation of impurities, corrosion resistance, temperature) and economical (evaporation is expensive but transporting water is as well) reasons, the phosphoric commercial grade has been set at 54%. This means, that depending on the production process, the acid coming out from the reactor tanks must be concentrated in 1 to 3 evaporation stages.

Through the years, many types of processes have been developed for concentrating phosphoric acid. Originally, submerged combustion concentrators where gas or fuel was burned directly in a pool of phosphoric acid and caused the concentration of the acid. These units were extremely pollutive and paved the way to vacuum concentrators. Natural circulation evaporators were used for a while until the actual design was adopted, i.e. forced circulation evaporators. The typical evaporation stages consist of an axial pump, a heat exchanger and a flash tank. The largest axial pumps can convey up to 12,000 m^3/h (50,000 gal/min). The pump casing and impeller are usually either in Sanicro 28 or Hastelloy G30. The largest heat exchangers can have up to 1000 tubes, be 10 meters (33') long and use up to 30 tons of steam per hour. The piping and conical headers are usually rubber lined. Bromobutyl or chlorobutyl rubber is usually the material of choice because of its temperature resistance. The flash tank is connected to a vacuum group. The absolute pressure in the flash tank is usually around 90 to 100 mbar while the acid boils between 92 and 95ºC. Vacuum evaporators are usually heated by steam which is a by product of the sulfuric acid production. Concentration of phosphoric acid is made in single-effect evaporators where approximately 800 kg of steam is required per ton of evaporation. Depending of the initial and final stage of concentration of phosphoric acid, the steam consumption can be as much as 2,5 to 3 tons of low-pressure steam per ton of 54% P_2O_5 produced.



The amount of water to be evaporated from phosphoric acid usually requires the use of multi stage evaporation units. Most commonly, two or three stage evaporators are used. A concentration level ranging from 35 to 39 % P_2O_5 is typically reached after the first stage, 44 to 46 % P_2O_5 after the second one and 54 % P_2O_5 after the third one. Typically the first stage can handle twice as much evaporation as the third one because it can operate at pressure considerably higher.

The key issue in phosphoric acid evaporators is scaling. Despite the temperature rise, the evaporation of water causes the supersaturation of gypsum that deposits on the tube surface. Heat transfer coefficients measured in phosphoric acid evaporators vary from 1000 when clean down to 500 W/m.K when the unit is completely fouled and requires cleaning.

2. Use of Synthetic Resin Impregnated Graphite

Synthetic resin impregnated graphite was selected for the manufacture of phosphoric acid evaporators because of its almost universal corrosion resistance to acids and halogenides. Chemically pure phosphoric acid by itself is a relatively mild acid. The Pkas of Phosphoric acid are 2,12, 7,21 and 12,67. But what makes industrial phosphoric acid corrosive is not the acid by itself but the impurities it contains, mostly chlorides and fluorides. Depending on the origin of the phosphate rock, the produced phosphoric acid contains more or less corrosive impurities. Synthetic resin impregnated graphite can handle the corrosiveness of green phosphoric acid and can be operated at high temperatures up to 200ºC (392 F).

Synthetic graphite is manufactured from crude oil cokes and pitch. The pasty mixture is shaped into monolithic blocks or tubes. Tubes are extruded whereas blocks are usually vibration molded. The shape is then carbonized at 900ºC (1650 F)for a few hours and then fully graphitised at 2900ºC (5250 F) for several days. The block or tubes are then impregnated with synthetic resin that is then polymerized to render them totally impervious to gases and fluids.

The resulting material is fully corrosion resistant to most common acids (sulfuric acid, hydrochloric acid and of course industrial phosphoric acid) and has a very high thermal conductivity of around 80 W/m.K for tubes or 140 W/m.K for blocks when totally graphitised. The tube wall is quite thick, 6 mm (1/4”) and the individual tubes are 3 meters (10’) long.

3. Historical use of Graphite Block Heat Exchangers:

Historically, graphite block heat exchangers have been used. In this equipment, the heat transfer takes place in solid synthetic resin impregnated graphite blocks with a crosswise arrangement of drilled flow passages for the product and service side. The size of the blocks depends on the process flow. Several blocks are assembled to form a column which provides the required heat exchange area in a single unit. The blocks are arranged in such a way that the product passages align with one another. As a result, the product comes into contact only with the corrosion-resistant synthetic resin impregnated graphite material.

The product flowing through the axial passages is collected in a top and bottom header at the heat exchanger inlet and outlet. A steel shell firmly secured to the base plate surrounds the space around the block column. The joints between base plate and bottom header/steel shell are sealed with gaskets. The whole block column is secured by bracing the top pressure plate against the steel shell. The joint between the steel shell and the top header is sealed e.g. by an O-ring to allow free movement of the shell. The difference in thermal expansion between graphite and steel is compensated for by helical compression springs. As a rule, the corrosive medium flows through the axial passages. The steam, in the shell space, passes through the radial passages. A baffle cage produces forced flow deflection on the service side.

The key advantage of the graphite block heat exchanger is their modularity and the possibility to replace damaged blocks. Heat exchanger surface can be increased by increasing the number of blocks. Damaged blocks can be individually tested and replaced on site by an experienced maintenance crew. On the other hand, the block heat exchanger design should also some limitations in terms of heat transfer efficiency and resistance to their and mechanical shocks. In case of damaged block, the whole unit shall be disassembled, the cracked block must be replaced and the whole unit shall be regasketed thus requiring a 24 to 48 hours shutdown.

As the evaporation units have become larger and larger, larger diameter blocks have become a necessity. The manufacturing process of graphite, i.e. vibration molding, has the adverse effect of becoming quite costly when the diameter of the block increases… thus causing the block heat exchanger design to become less competitive against the shell and tube technology.

This is also without mentioning the fact that because service channels are horizontal the condensate removal can become problematic as the flow rate of steam increases. Attempts to resolve this limitation with sloped service channels and small ejectors have shown some limited success and have slightly shifted upward the limit above which block heat exchanger are not suitable anymore in phosphoric acid evaporation applications.

4. Use of Graphite Shell and Tubes Heat Exchangers:

As the size of phosphoric acid plants increased, came the need for larger and larger evaporators. As the synthetic resin impregnated graphite block heat exchangers reached their operational limits, phosphoric acid producers implemented more and more graphite shell and tube heat exchangers. Rapidly, however, three major issues were revealed in operation. The first one was tubes cracking, the second was the splitting of tube sheets into two pieces, and the third one was the erosion of the tube sheet at the heat exchanger entrance.

Tube cracking:

The brittleness of the tubes is more or less inherent to the nature of the synthetic resin impregnated graphite material. This being said, there are many ways to increase the tubes sturdiness while also reducing the occurrence of the cracking causes.

The main causes of tube cracking are, by order of decreasing importance, steam hammering, thermal shocks, fouling, mechanical erosion caused by poor maintenance procedures, cutting by steel baffles , shearing stresses, aging, and operational erosion.

- Steam hammering occurs when butterfly valves are being open or closed too rapidly, when sub-cooled condensates stagnate in steam lines, when condensates lines are not properly designed (too small diameter, climbing or horizontal pipes), or when steam lines are not drained before start-up.

- Thermal shocks occur when the heat exchanger is being started too rapidly or when the propeller pump shuts down and restarts.

- Fouling can also cause tubes to crack. When the fooling layer become too thick, solid and start to dry, the expansion of the gypsum material causes the tubes to be submitted to forces that cause the tube cracking.

- Mechanical erosion can be caused by inappropriate maintenance procedures. High pressure water blasters, that are commonly used to descale the gypsum deposit inside of the tubes can easily erode the graphite tubes wall if not properly used thus causing the tube walls to become thinner and ultimately the tube to crack.

- Cutting by steel baffles occurs when steel baffles on steam side vibrate and slowly erode the graphite tube from the outside. In practice, tubes are sawed by the steel or stainless steel baffles.

- Shearing stresses occur when the tube bundle is not properly installed within the shell, when the shell flanges are not strictly parallel, or when the tube bundle is being “twisted”. Under these conditions, a shearing stress is exerted on the tubes which can break usually at the joint with the tube sheet.

- Aging causes the tubes to lose some of their mechanical strength. The life expectancy of a graphite shell and tube heat exchanger should not exceed 12 to 15 years of operation.

- Operational erosion occurs when the tube side velocity is too high. The maximum allowable velocity depends mostly on the phosphate rock used. With phosphate rocks that contain a lot of silica, erosion might occur from 2,7 m/s (9'/s) whereas with some igneous rocks erosion might not occur until 4,5 m/s (15'/s). In most cases, the erosion doesn't actually occur within the tubes but at the tube sheet surface.

Tube sheet cracking:

- Graphite shell and tube heat exchanger users also encounter tube sheet cracking. What normally happens is a radial split of the tube sheet in two parts signifying the end of the heat exchanger life. The main causes of tube sheet cracking are over-tightening, non monolithic tube sheets and aging.

- Over- or uneven-tightening occurs when maintenance crews do not pay enough attention to the tightening torque, use improper gaskets or do not respect the recommended good practices for tightening (criss-cross fashion). This also happens when an improper gasket material is being used.

- Tube sheet splitting is more likely to happen when non-monolithic tube sheets are being used. Aging causes the cement between the individual blocks to loose its mechanical strength and causes ultimately the splitting of the individual blocks that constitutes the tube sheet.

- Aging affects also monolithic tube sheets by causing the mechanical properties of the synthetic resin impregnated graphite block to slowly decrease. When the mechanical constraints on the block become too strong, the tube sheet is split into two pieces.

Erosion of the tube sheet at the heat exchanger entrance:

- Erosion of the tube sheet (at the entrance into the tube) might occur when the process fluid velocity is too high. The maximum allowable velocity depends mostly on the phosphate rock used. With phosphate rocks that contain a lot of silica and not enough fluorides to totally dissolve it. Erosion might occur from 2,7 m/s (9'/s) whereas with igneous rocks erosion might not occur until 4,5 m/s (15'/s).

5. Carbon Fiber Reinforced Graphite:

Based on the mechanical features of the synthetic resin impregnated graphite, we have developed and implemented several technologies to offset the limitations of the material.

Synthetic resin impregnated graphite is a composite material that is made of about 85% of graphite grains and about 15% of synthetic resin. The synthetic resin has two functions. First, it makes the material impervious. Second, it enhances its mechanical properties. After synthetic resin impregnation, the graphite material is actually two times stronger than before impregnation. All the voids are totally filled with resin and the material is then 100% solid.

The compressive strength of graphite is some 3 to 5 times its tensile strength. This fact is of major significance when graphite is used as a construction material for chemical process equipment. For such applications the rules that apply to ceramic materials must be observed. The relative fatigue strength of impregnated graphite under alternate bending stresses is higher than that of most metals. So, the material is known to have a limited mechanical resistance in tension. But, on the other hand, it has a pretty good mechanical resistance in compression. Based on this feature, we developed a technology that maintains the graphite tubes and tube sheets at all times under compression thus significantly enhancing its mechanical resistance.

Tubes:

The technology consists in wrapping the impregnated graphite tubes with a criss cross pattern of carbon fiber. The adhesion of the carbon fiber to the graphite material is ensured by dipping the fiber into synthetic resin before applying it. Carbon fiber presents two main advantages. First, it is extremely strong. The strength of the carbon fiber render possible the pre-tensioning of the fiber before applying it thus maintaining the graphite under compression at all time. Second, it has a negative expansion rate thus meaning that the carbon fiber shrinks when the temperature rises. As a consequence, at elevated temperatures the compression strength applied on the graphite material is even stronger than at lower temperatures.

The bursting pressure of a standard synthetic resin impregnated graphite tube at 20ºC (70 F) is 80 bar (1200 psi). This value decreases to 75 bar when the temperature rises to 150ºC (302 F). Oppositely, when the tube is reinforced with carbon fiber, the bursting pressure is at 110 bar (1650 psi) at 20ºC (70 F). When the temperature reaches 150ºC (302 F), the bursting pressure rises even further to 120 bar (1800 psi).

The elastic behavior of the carbon fiber ensures that the tension on the reinforcement is retained even under sharply fluctuating load or stress surges. No fatigue is experienced.

The reinforcement does not impair resistance to corrosion because the chemical resistance of the reinforcement is identical to that of synthetic resin-impregnated graphite.

The resistance to mechanical stresses such as pressure hammering is relatively 2,5 times higher with carbon fiber reinforced tubes as with standard tubes. In practice, users utilizing carbon fiber reinforced tube have commonly experienced 20 times less cracked tubes than with standard graphite tubes.

The carbon fiber reinforcement also prevents the tube from completely opening in case of a crack. The leakage resistance pressure can reach up to 3 bar (45 psi) and is greater at higher temperatures than at room temperature. During operation, this means that a carbon fiber reinforced tube can work without a significant leak having a differential pressure between the service and the process side of up to 3 bar (45 psi). In practice, this means that a unit with a cracked tube doesn’t have to be stopped right away and can still operate for several days without any major difficulty. Because of the higher pressure on service side, the operators might actually not even detect the leak until they stop the unit and perform an air pressure test on process side. In all instances, the reinforcement prevents any breakout from the tube and a consequent escape of product in large quantities. The shell suffers virtually no corrosion. Usually, the equipment can continue in operation without interruption until the next planned shutdown.

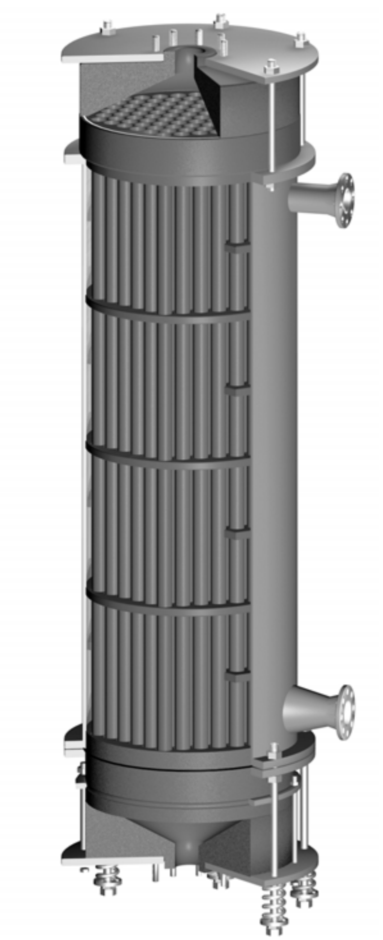
Tube sheets:

As far as tube sheets are concerned, the carbon fiber is simply wound around it. The effect of the carbon fiber on the tube sheet is similar to the one that it has on the tubes. It maintains the graphite under compression at all time and prevents it from splitting into several pieces.

We recommend the carbon fiber reinforcement of any tube sheet that has a diameter larger than 1,2 m (4”) and considers it as a necessity when the tube sheet is not built out of a single monolithic piece of graphite. The so-called segmented tube sheets, meaning tube sheet made out of several graphite blocks that are cemented together, over 1,8 m (6’) in diameter must be carbon fiber wound in order to maintain their integrity for the long-term.

6. State of the Art Construction:

With years of experience in operation, we have implemented several measures to improve significantly the reliability of the graphite shell and tube heat exchangers.



Graphite:

To minimize the effect of aging and corrosion, the graphite that is used for the manufacturing of process equipment must have the following properties. It should be mechanically strong and be completely impregnated. In order to achieve this result, we use the appropriate grain sizes distribution of coke and graphite powders to enhance the mechanical properties. The combination of larger and small grains is actually what brings the mechanical strength to the material while also resulting in a very high thermal conductivity. The thermal conductivity of the graphite tubes reaches 80 W/m.K. A high thermal conductivity of the graphite material is one of the keys to the heat exchanger efficiency.

Baffles positioning rods:

First of all, all the baffles positioning rods that were originally designed in carbon steel or stainless steel are now in graphite. The exact same material as the tubes is used. This has the major advantage of having the same expansion rate as the tubes themselves. This means that the tube bundle is not put under stress when the temperature varies.

Baffles:

The baffles are now exclusively made out of impregnated graphite. The use of graphite instead of carbon steel, stainless steel or polypropylene presents numerous advantages. First of all, the graphite baffles do not have sharp edges and can consequently not cut the graphite tubes in cases of friction or vibration. Secondly, the baffles are made of a softer graphite than the tubes thus meaning that in case of friction, the baffles might be preferentially eroded and not the tubes. Thirdly, graphite expands much less than steel, stainless steel or polypropylene thus enabling us to minimize the gaps between the baffles and the shell.

Tubes:

As a rule for the manufacturing of phosphoric acid evaporators, the use of carbon fiber reinforced tubes is strongly recommended. These tubes are fully graphitized thus leading to a thermal conductivity of approximately 80 W/m.K.

Tube / tube cementing:

The tubes are manufactured to a length of 3 m (10’). Since most phosphoric acid evaporators are much longer than that, tubes pieces must be cemented together to reach the required tube length. In order to preserve the mechanical strength of the graphite tube and to prevent bending a very special male / female connection shape has been developed. Actually, the cementing factor is 1 thus meaning that during bursting tests, we do not see more failure at the joint than anywhere else.

Tube / tube sheet cementing:

Tubes and tube sheet are cemented together in one operation. A conical male (tube) / female (tube sheet) connection is cemented. The cement is a mix of synthetic resin and graphite powder. The tube bundle is then heated to the cement polymerization temperature. Too much cement could result into stresses on the tubes. Not enough cement might result into leaks. Therefore it is important to apply the right quantity of cement.

Tube sheets

As a rule all tube sheets are made out of one monolithic piece of graphite up to 1,8 m (6') in diameter. Above this diameter, tube sheets have to be manufactured out of several pieces of graphite that are machined according to a very special pattern and cemented together. All tube sheets above 1,2 m (4') in diameter are carbon fiber wound.

Some manufacturers put steel shrouds around their graphite tube sheets and claim that it brings some additional strength. Our own experience shows that the use of a steel or stainless steel shroud in lieu of the carbon fiber reinforcement is totally useless from a mechanical standpoint because of the expansion rate of the steel that is much higher than the one of graphite. As a consequence, the steel shroud becomes loose around the graphite tube sheet as soon as the temperature rises and consequently doesn't bring any additional strength to the material.

The thickness of the tube sheet is also a predetermining factor in the lifetime of the equipment. Basically speaking the thicker the tube sheet the better.

O'ring gasket:

Instead of using packing, the use of an O'ring gasket between the floating tube sheet and the shell has several advantages. First, it allows easy sliding of the tube sheet into the shell as the equipment temperature rises. Secondly, it diminishes the stress on the tube sheet thanks to a better distribution of the tightening forces.

Expansion system:

An expansion compensation system is rendered necessary by the strong differential expansion between the graphite tubes and the steel shell. Compression springs allow the movement of the tube bundle into the shell while it maintains it at all times under compression. Belleville washers are not used anymore on large graphite heat exchangers.

Protection against erosion:

In order to prevent tube sheet erosion, ceramic coated inserts can be cemented at the inlet of each tube. The hardness of the ceramic inserts is such that no erosion can be observed in operation even when the green acid contains a lot of silica.

Steam distribution belt:

When the steam flow rate into the shell is high, i.e. above 10 ton/hour, we recommend having a 360º distribution belt around the main shell with large entrance windows to better distribute the steam, prevent excessive steam velocity, prevent droplet impact and optimize the thermal exchange. By better distributing the steam in the shell, a 360º distribution belt might also reduce the effect of steam hammering on the tubes.

Stainless steel or Uranus B6 shell bottom:

Having the bottom 1 to 1,5m section of the shell made out of stainless steel or Hastelloy B6??? can make sense. This prevents excessive corrosion of the shell bottom and preserves its integrity in case of tube failure.

A few phosphoric acid producers have even implemented shells completely in stainless steel. Whether it makes sense or not mostly depends on the external environment. In humid, hot and acid fume environments, it is actually a pretty intelligent choice.

7. Operational recommendations:

Heat exchanger sizing:

The proper sizing of the heat exchanger is one of the key parameter to ensure smooth and reliable operations. Excessive fouling factors might lead for example to slow fluid velocities and cause poor heat exchange performance. The proper determination of the acid viscosity is also an important parameter since it can affect significantly the film coefficient on the process side. Neither aggressiveness nor conservatism are actually beneficial when heat exchanger sizing is in question. Realistic fluids properties (viscosity is a very important factor here) should be taken to size the evaporator.

Steam quality:

In most of the phosphoric acid producing units in the world, the steam network is fed by the steam generation unit of the sulfuric acid plant. The steam is usually pretty clean and is produced at pressures between 4 (60 psi) and 10 bar (150 psi). The steam usually contains a limited amount of non-condensables.

Control valves:

On large units that use up to 30 tons of steam per hour, it is recommended to implement two control valves of different sizes in parallel, for example 24” main valve and 12” secondary valve in parallel, in order to make the start-up procedure more smooth. This configuration enables a progressive heat up of the shell and prevents thermal stresses on the tube bundle and tube sheets.

When the high-pressure steam network is used to feed the heat exchanger, the control valves act as a pressure reducer thus meaning that the saturated steam before the valves become superheated after the valve. As a consequence, when the steam dew point is far below the actual steam temperature after the valve, it is recommended to desuperheat the steam by adding water to the flow. It is essential that the steam arrives saturated into the heat exchanger in order to enhance its performance and also to prevent excessive fouling.

Steam lines:

The design of the steam lines is extremely important for the reliability of the operation. They should be designed according to good steam handling practice, equipped with steam straps at the lowest points, filtered, and properly insulated.

Condensates lines:

The proper removal of the condensate from the shell is also one of the key factors to prevent steam hammering. Condensate lines shall be biphasic at all times. Ttis means that the liquid condensate and the steam must always be in equilibrium. The condensate lines must be either vertical or sloped and must be large enough to prevent the accumulation of steam pockets between condensate pockets. In any case, condensate lines shall neither be horizontal nor rising. Condensate lines shall be fitted with drain valves at the lowest points.

Start-up procedures:

The start-up sequence is the most critical for the heat exchanger. Before anything else, the axial pump on the green acid loop must be started. The condensate and steam lines must be totally drained. The steam lines must be heated-up while the control valve remains closed. The last drain valve before the control valves must be kept open until only saturated steam comes out. Then, all the drain valves must be closed and the steam must be progressively introduced into the heat exchanger shell. Within the first 10 minutes, the smaller valves should open from 0 to 100%. Then the main valve should be slowly opened at a such a rate that the nominal point would be reached within 30 to 50 minutes depending on the size of the equipment. The temperature difference between the shell and the process side should be kept under 50ºC (100F) at all times to prevent fouling and thermal stresses. The shell should be vented in order to remove the non-condensables that might have accumulated within the steam network.

Operations:

During operation, the pressure drop and the overall heat transfer coefficient must be carefully monitored to prevent the fouling layer from becoming too thick. As the predetermined lower overall heat transfer coefficient limit is reached, the heat exchanger must be chemically cleaned to prevent the further build-up of a gypsum layer that might become very difficult to remove.

The temperature difference between the process and service side must not be too high. Ideally, it should not exceed 25ºC (50F) to 30ºC (60F) to prevent rapid fouling.

The temperature difference between the heat exchanger inlet and outlet should also be as low as possible. 3 to 5ºC is actually recommended since an excessive temperature difference between the inlet and the outlet of the equipment might also lead to a more rapid fouling.

Use of softening agents

Some phosphoric acid producers have added anionic surfactants directly into the evaporation loop in order to prevent the hardening of the gypsum layer. Sodium TriPolyPhosphate (STPP) has for example been used and has given interesting results. Results may vary with the type of phosphate rock used and the process conditions.

Chemical cleaning:

Chemical cleaning is the most recommended cleaning method when graphite tubes are being used. It has several advantages over mechanical cleaning. First, there is no need to disassemble the equipment. Secondly, it can be very efficient if done early enough, thus meaning before the gypsum layer becomes too thick. Thirdly, if done properly, it slows down the fouling during the next production cycle because it actually reduces the number of remaining gypsum crystal seeds.

Numerous chemicals are used to clean the graphite tubes fouled with gypsum: hot water, diluted sulfuric acid, hydrofluoric acid, or chelants. Calcium complexants such as EDTA (ethylenediaminetetraacetic acid) or its biodegradable substitute SS’-EDDS (S, S'-ethylenediaminedisuccinic acid) have been successfully used by some producers around the world.

Impurities can severely affect the crystal structure of gypsum. The presence of strontium for example, mostly found in igneous phosphates, is known as being a significant drawback since it causes the gypsum layer to be quite compact and pretty difficult to remove.

Mechanical cleaning:

Mechanical cleaning is widely used to remove the gypsum layer from the tube surface. The use of adapted mechanical cleaning procedures with self-progressing rotating water jet low pressure blasters (maximum 200 bar, 3000 psi) mounted on a flexible hose preserves the integrity of the tubes by preventing their internal erosion.

The use of high pressure non-rotating water blasters mounted on lances is to be totally forbidden.

For the best cleaning results and the least damage to the equipment, the mechanical cleaning operation is to be performed by an experienced crew.

Equipment lifetime:

The equipment lifetime depends strongly on the operation conditions. However, it is wise to say that after 12 to 15 years in operation, a graphite shell and tube heat exchanger reaches the end of its life. After that time, the need for unscheduled maintenance is likely to increase exponentially. This being said, numerous heat exchangers that we sold in the early 1980's with carbon fiber reinforced tubes are still in operation today with a limited number of broken tubes.

8. Conclusions:

The carbon fiber reinforced synthetic resin impregnated tubes bring a lot of additional reliability to the phosphoric acid evaporation process. The observed improvements are particularly significant when the steam and condensate systems are not properly designed or harshly operated. Nowadays, we supply nearly all large phosphoric acid evaporators with carbon fiber-reinforced tubes and tube sheets.

The industrial experience have shown that in evaporation units where carbon fiber reinforced graphite tubes have been implemented, where the steam and condensate lines are properly designed, and where smooth start-up and shutdown procedures have been totally computerized it is possible to achieve a zero failure rate for the first 5 years of operation at least. It has also been proven that the quality of the steam, the way steam and condensate piping network are designed, and moreover the way the evaporation units are operated are of primary importance for the reliability of the operations.

The use of adapted mechanical cleaning procedures with self-progressing rotating water jet low pressure blasters mounted on a hose preserves the integrity of the tubes by preventing their internal erosion.

Besides, the use of chemical cleaning is recommended. The use of chelants such as EDTA or its biodegradable isomer SS'-EDDS can give astonishing results and limit the need to resort to mechanical cleaning. Besides, the addition of softening agents, such as Sodium TriPolyPhosphate (STPP) for example, in the evaporation loop prevents the fouling layer from hardening too much during operation. The amphiphile nature of STPP also reduces the deposit of gypsum at the tube surface.

As far as the heat exchanger design is concerned, the implementation of carbon fiber reinforced tube sheets, a 360º steam distribution belt, carbon fiber reinforced tubes, graphite baffles and ceramic coated inserts provides the best possible chance to increase the reliability of existing evaporation units.

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