Graphite Plate Heat Exchangers as Energy Saving Tool for Corrosive Media Duties

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The phenomenon of corrosion is one of the most common difficult problems for many heat exchangers in industrial processes. High grade alloy and exotic metals in many cases are of excellent resistance to corrosive fluid attack, but there are some cases where even these materials reach their limits. A number of nonmetallic materials for heat exchangers such as Teflon, borosilicate, glass etc have limited range of application because of their low heat transfer properties and specific mechanical characteristics.

The important place among nonmetallic heat exchangers is occupied with graphite heat exchangers used in acid cooling and heating, treatment of electrolytes, pickling liquors heating, heat recovery and cooling of dangerous waste fluids and so on. The overview of types of graphite heat exchangers is presented. It is outlined the development and implementation of new type of graphite heat exchangers – high effective corrosion resistant plate and frame units. It is an important step in extension of duties of plate heat exchangers. The physical and mechanical properties of graphite composite material of plates are presented and main features of graphite plate heat exchangers are discussed.

The case study for energy saving retrofit of heating system of continues pickling line is presented. The principles of heat substation based on graphite plate heat exchanger are discussed.

1. Basic concepts of graphite heat exchangers

1.1 Graphite based materials for heat exchangers

Many industrial processes are dealing with high corrosive process fluids, such are chemical and fertilizer production, surface treatment of metals, petrochemical processing, fine chemical and pharmaceutical production, heat recovery and cooling of dangerous waste fluids in environment protection.

Heat exchangers are the necessary hardware for industrial processes and corrosion resistance is vital for these units. Even the use of high grade and exotic alloys and metals reach their limit for number of corrosive fluids especially at high temperatures.

For today one of the solutions that let to overcome corrosion problems is the use of graphite as the material for heat exchangers. Graphite is finding many applications in different industries for handling the corrosive media. Such properties as chemical inertness, high thermal conductivity and good machining are well suited for heat transfer equipment. The resistance to oxidizing media highly increases by impregnation that improves characteristics of material. The certain grades of graphite are suitable for heat exchangers manufacturing, with appropriate dense structures and low porosity (Hills D.E.G., 1971). The porosity can be limited by impregnation with synthetic resins, polyesters, PTFE, etc. The type of impregnator, the impregnation technique and curing define possible characteristics of heat exchanger and its working life.

For impregnated graphite used for process equipment the corrosion resistance is defined mainly by corrosionability and thermal shrink ability of impregnator as well as by the pore structure of the graphite. Because of high thermal conductivity impregnated graphite is an excellent material of the heat exchangers; the synthetic impregnator does not impair thermal conductivity. In this paper we consider impregnated graphite materials and heat exchangers on their base. Two well-known companies - Sigri Great Lakes (SGL) Carbon Group (Germany) and Groupe Carbone Lorraine (France) produce the range of such equipment based on impregnated graphite materials DIABON® and GRAPHILOR® brands.

The graphite heat exchangers from a number of manufacturers may be divided in three types: shell and tube, block type and plate graphite units.

1.2 Shell and tube graphite heat exchangers

The usual shell and tube graphite unit consists of exchanger tubes, tube sheets or plates of graphite because the full corrosion resistance of graphite is needed on the tube side. The shell may be metal or lined metal.

Standard maximum design pressure is 6 bar gauge and maximum temperature is 180ºC. The maximum tube length may reach 9 m, inner diameter 37 mm. Surface area of standard single unit may be 500 m^2 and more.

To enlarge the pressure duty the reinforcement of components is used. SGL Carbon developed and implemented the carbon fiber reinforcement of tubes, tube sheets and headers with SIGRAFIL® HF fibers. The tubes became more resistant to steam hammering and process pressure. The resistance to surges for tubes increases about 2.5 times (SGL Carbon Group, 2006).

Shell and tube graphite heat exchangers are mainly used in cases where very large throughputs are required. One of such cases is steam heating of phosphoric acid before evaporation chamber in concentration stage of conventional dehydrate process in wet method production (Beveridge G.S., Hill R.G., 1968).

1.3 Block type graphite heat exchangers

Block type units are compact and usually consist of graphite block or blocks, perforated with rows of parallel holes for conveying the two fluids. A number of blocks are built as the core of heat exchanger. The plurality of block types for graphite heat exchangers can be approximately divided in three groups:

cubic block heat exchangers;

cylindrical or cartridge graphite heat exchangers;

monoblock graphic heat exchangers.

All block units are compact and have additional advantages:

suitability for corrosive media on both sides that make their use possible to recuperative duties; high thermal efficiency; possibility to clean and replace each block; for multiblock core possibility to increase or decrease the heat transfer area by adding or removing blocks.

Cubic block unit consists of graphite block core. Each lateral face of block is drilled with parallel cylindrical holes for streams flow. The rows of holes are alternated through the thickness of the block. The core is inserted between headers with inlet/outlet ports. Headers may be equipped with baffles to enable arrangement of multipass flows. The surface of such units may reach 50-260 m^2 , standard maximum working pressure is 5-7 bars (each side), design temperature 175-180ºC. Materials – graphite impregnated with phenol resin or TFE (PTFE) (SGL Carbon Group, 2006; Groupe Carbone Lorraine).

Cylindrical block heat exchanger consists of impregnated graphite blocks that incorporate axial and radial drillings or passages. The blocks are stacked upon a base with corrosion resistant gasket between each block.

The example of one of the most extensively used cylindrical block heat exchanger is series M POLYBLOC graphite units manufactured by Group Carbone Lorraine. The main feature of series M units is in the arrangement of the drilled holes and the centrifugal-centripetal flow characteristics. The radial drillings are at the angle to the radius and open to the central chamber. Such layout promotes the turbulence and decreases risk of fouling. Multipass arrangement lets to obtain total counterflow of fluids.

Such units let to reach surface area up to 500-600 m^2 depending on type. Maximum working pressure for standard units are 7 bar and maximum temperature is 200ºC (SGL Carbon Group, 2006). They may be used as interchangers, heaters/coolers, condensers. Important applications are: pickling lines, phosphoric and super phosphoric acid production, extraction with solvent of pure phosphoric acid, etc. Block material usually is similar as for cubic block graphite units.

Monoblock heat exchangers are made from single monolithic impregnated graphite block that includes impregnated baffles on each fluid side. The graphite block is sealed on four faces with PTFE lined steel plates that are braced together. The heat exchanger area may be up to 260 m^2, maximum working pressure is 10 bar, maximum permissible temperature is 200ºC (SGL Carbon Group, 2006). Field of application: interchangers, heaters and coolers.

1.4 Plate graphite heat exchangers

Plate graphite heat exchanger is the variant of the traditional plate and frame design with plates of impregnated graphite, the development of Alfa-Laval and SGL Carbon Group. This heat exchanger combines high corrosion resistance with high heat transfer efficiency in compact and robust construction. The sealant is also of high corrosion resistance and thermally stable. It is a self vulcanizing fluoroelastomer that is disposed at the edges of plate and around two collector holes to form a continuous seal once the plate pack is compressed in the frame.

To protect the frame/pressure plates and the nozzles LICUFLON® lining is used. Interplate sealing is applied about 20 mm wide sealing strips on the graphite plates by compressing of soft fluoroelastomer that is compressed to a film thickness about 0.2 mm after compression the plate pack (SGL Carbon Groupe, 2006).

For such plate heat exchangers the plates are manufactured of DIABON® F100, DIABON® NS1 and NS2. DIABON® F100 is the trade mark for a fluoroplastic bonded, nonporous fine grain graphite with high homogenous structure of material. DIABON® F100 plates are made with herringbone corrugated patterns like usual corrugated metal plates, see Fig. 1.

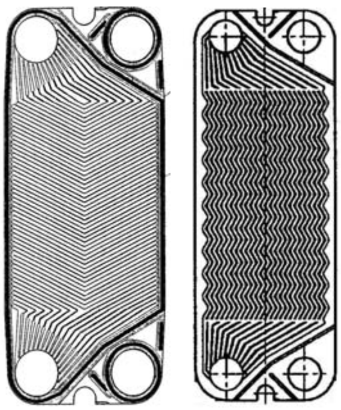

Figure 1: a) cross corrugated DIABON® F100 plate; b) free flow DIABON® NS1 plates

DIABON® NS1, NS2 plates have one side flat and smooth and on another side the plurality of wavy parallel channels. See Fig. 2b. The free flow channel results with adjacent plates in the pack.
Three types of DIABON® Plate Heat exchangers are manufactured. The biggest S10/S10 – N types may have maximum 130 plates on DIABON® F100 (area per plate 0.4 m^2) and 96 DIABON® NS1, NS2 plates (area per plate 0.304 m^2) (SGL Carbon Groupe, 2006).

1.5 Graphite Heat Exchanger Limitations

Despite of wide range of duties with corrosive media graphite heat exchangers cannot handle everything. There are problematic media whith high oxidation potential (chromic acid, sulphuric acid>90%, oleum, chlorosulfonic acid), some acid mixtures (aqua regia, nitric/hydrochloric or hydrofluoric acid > 20%), elemental chlorine and bromine in aqueous solutions, alkalis (caustic potash or sodium solutions > 10%), bleach liquors (calcium or sodium hypochlorite), organic solvents with high polarity. DIABON® F100 plate heat exchanger is not recommended for two phase applications.

2. GRAPHITE HEAT EXCHANGERS FOR PICKLING PROCESSES: CASE STORY

The pickling process is very important for preparation of metal product to further treatment and processing. It is chemical process of removing films of cinder and corrosion products from metal surface. The pickling process has the great significance in steelworks for treatment of carbon and stainless steels. The pickling process mainly implemented in pickling vats filled with pickling liquor and equipped for immersion of metal products to be treated. The nature of pickling liquor depends on kind of metal or alloy. For example, for carbon steel pickling the solution of sulfuric and hydrochloric acids are used, for pickling of some stainless steels the mixture solution of nitric and HF acids is used. The successful pickling process requires high temperatures, for example, for carbon steel pickling it is about 90ºC, so the pickling liquor must be heated during the process. Pickling may be batch and continuous. In batch processes the stacks of details are immersed in vat for required time. In continuous processes the bulk of metal is going through pickling vats for a long time. The pickling time defines the linear velocity of metal moving and pickling liquor is continuously refreshed without stopping the process. There are three ways of heating the pickling liquor:

- through immersed in vats heat exchange devices;
- with injection of steam into vats;
- in external heat exchanger with steam or superheated water.

For carbon steel pickling at Ukrainian steelworks second way is usually used either for continuous or batch processes. In case of 10÷20% H_2SO_4 solution as pickling liquor main problems are the decrease of H_2SO_4 concentration and excess energy consumption at steam superheating. The first and third ways are more attractive from viewpoint of saving of acid consumption. But the first way of heating is not effective because of low heat transfer effectiveness, especially for continuous pickling lines of large capacities. The third way has the higher heat transfer effectiveness caused by forced convection heat transfer in external heat exchanger and good mixing of pickling liquor in vats due to forced circulation of liquor.

Our case is the first step in the scope of energy and resources saving retrofit of pickling lines in Ukrainian steelworks. The possibility of using of the graphite plate exchangers DIABON® for steel pickling process was investigated. The investigations were carried out on one of the biggest continuous pickling lines for sheet carbon steel pickling. Diluted 10÷24% H_2SO_4 was used as pickling liquor with it regeneration (removing green vitriol – $FeSO_4 \cdot 7H_2O$) in special unit. The heating of pickling liquor is taking place in four 50 m^3 vats by superheated steam with temperature 250÷270ºC through special tubes with nozzles immersed into vats. It dilutes the liquor, demands additional debit of H_2SO_4 and overloads the regeneration station.

If the external heat exchanger of surface type is used it is no necessity to heat the liquor with high potential superheated steam. It is just enough to use saturated steam with temperature 130÷150ºC. The forced circulation of liquor from vat through heat exchanger was made by fluoroplastic centrifugal pump. The graphite plate heat exchanger DIABON® NS1 of 4.5 m^2 was selected as experimental unit.

The conditions of the duty for experimental unit were according to operational parameters of existing pickling line as follows:

temperature of saturated steam – 110÷140ºC;

concentration of H_2SO_4 in pickling liquor: 20%;

circulation of pickling liquor trough heat exchanger: 20÷40 m^3/h;

temperature of pickling liquor on inlet of heat exchanger: 81÷94ºC.

The strict limitation on liquor heating was 100÷102ºC on outlet of heat exchanger to prevent the formation of $FeSO_4$ monohydrate scaling in heat exchanger and pickling vat. The experimental values of overall heat transfer coefficients were 1900÷2200 W/sq.m.K. The tests have shown the possibility to keep the demanded temperature of pickling liquor during the process with saturated low potential steam of temperatures as low as 110÷120ºC. After tests the plate heat exchanger was dismantled and surface area inspected. Because of relatively high velocities of pickling liquor the surface was clean without any traces of $FeSO_4$ monohydrate scaling.

Conclusion

The modern trends in graphite heat exchangers development are the increase of surface area per unit, implementation of new impregnated materials and reliability of constructions. There are possibilities to implement the plate graphite heat exchangers with enhanced surface area into existing industrial processes in Ukraine for energy saving projects implementation.

Acknowledgement

The support of EC Project ECOPHOS (contract № INCO-CT-2005-013359) is sincerely acknowledged.

References

Hills D.E.G. Graphite Heat Exchangers, 1971, Chemical Process Engineering, 52, 1.
DIABON® Shell and Tube Heat Exchangers. Process Technology. SGL Carbon Group materials 05 2006/1E, printed in Germany.
Beveridge G.S., Hill R.G., 1968, Chemical @ Process Engineering, 49, 8.
DIABON® Block Heat Exchangers. Process Technology. SGL Carbon Group materials 05 2006/1E, printed in Germany.
Cubic Exchangers made of GRAPHILOR®. Groupe Carbone Lorraine. Material EGC 325-1GB1030. Imprime en France- S.I.C. – CHATEANEUS sur LOIRE.
Polyblock Heat Exchangers in GRAPHILOR®. Groupe Carbon Lorraine. Material SM 101GB0040. Imprime en France- S.I.C. – CHATEANEUS sur LOIRE.
DIABON® LICUFLON® Plate Heat Exchangers-Superior by Design. Process Technology. SGL Carbon Groupe materials 05 2006/1E, printed in Germany.