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Research on Protective Measures to High-Temperature Corrosion of a Novel Energy-Saving Phosphorus Reaction Tower

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To recycle and utilize the reaction heat in the production of furnace grade phosphoric acid and to improve the security and economy of the whole production system, a novel phosphorus reaction tower with circulating water wall was developed on the basis of the analysis of present manufacturing process and equipment, and the mechanism of high-temperature corrosion was also analyzed according to experimental tests and operating conditions. Meanwhile, the measures of the whole life cycle anti-corrosion taken to new phosphorus reaction tower were proposed, considering multiple factors including design, manufacture, and operation. The research suggested that the fins close to phosphorus burner, heat exchange tubes toward phosphorus burner and the welds between fin and tube were dangerous zones to be corroded and should be given special protection. In addition, it has been proved that 390-440 °C surface temperature of water wall, local water cooling jacket around the oblique burner, plasma-sprayed ZrO_2 ceramic coating on heating surface, ultralow carbon austenitic stainless steel rich in Cr and Ni elements are beneficial to avoid the corrosion of high-temperature phosphoric acid and its polymer.

Keywords high-temperature corrosion, mechanism, phosphoric acid, protective measures, reaction tower

1. Introduction

Phosphoric acid, as an important chemical raw material, is widely used in the chemical, pharmaceutical, food, electronic, military, and other industries. With the rapid development both in industry and in economy in China, the high demands for phosphoric acid, especially highly-pure (Ref 1), are increasing day by day in the national market. Nowadays, the production of highly pure phosphoric acid mainly relies on furnace or reaction tower. Phosphorus extracted from crude ore is burnt to create mixed gas containing phosphoric pentoxide (P_2O_5) which is absorbed by water or attenuant acid, so as to gain highly pure phosphoric acid with different concentrations. The combustion of phosphorus is an aerobic reaction releasing strong light and heat. Usually, 1 kg phosphorus burned can generate about 24385 kJ heat (amount to the combustion heat of standard coal). Even if the excess air coefficient reaches 1.5, the temperature of mixed gas is still higher than 2200 °C. Due to the effect of such a high temperature, equipment will be eroded by P_2O_5 and its polymer, and the situation will become worse with the temperature rising. In order to lower the temperature and prevent corrosion, water cooling jacket is equipped with the conventional phosphorus reaction tower. The temperature of circular water in the intake and outlet of the traditional jacket is about 35 and 50-55 °C, respectively. Not only is it difficult to recover and utilize such low temperature waste heat, but also it requires the configurations of huge plate heat exchanger and additional steam boiler to cool circulating water and melt solid phosphorus. Direct consequences in this way are energy waste, high production cost, as well as heat pollution. Therefore, from the perspective of energy saving and environmental protection, it is necessary to improve and optimize the conventional phosphorus tower with cooling jacket. At present, a novel phosphorus tower with heat recovery has been put forward (Ref 2).

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2. Structure and Working Principle

The novel phosphorus tower is designed by integrating the combustion chamber with heat recovery components as shown in Fig. 1 (Ref 2), which is similar to a steam boiler. The combustion chamber is a hollow constructure consisting of conical heads and a series of heat-exchange tubes connected by 10 mm wide fins. Heat-exchange tubes are connected at their ends of the intake manifold and discharge manifold, respectively, which are circular pipes with a great number of evenly distributed radial holes. There is an insulated layer between the outer wall of phosphorus combustion chamber and the furnace shell. Compared with the conventional phosphorus tower, the new device with water cooling wall is characterized by the following aspects: (1) the shape and volume of combustion chamber of the novel phosphorus tower are the same as the conventional equipment. The installing position of burner relative to the previous whole device is uniform, so that new phosphorus tower can satisfy the production requirements of furnace grade phosphoric acid; (2) after turning water cooling jacket into water cooling wall, the waste heat released by the phosphorus combustion can be effectively recovered; (3) since the entire phosphorus tower is supported by skirt or suspended by steelwork, it is no surprise that the furnace body can expand upward or downward without constraint when heated. In addition, the ends of downtakes connected with drum and upper manifold, as well as the ends of collecting tubes connected with drum and lower manifold have elbows at their joints, which can compensate for thermal expansion effects.

During the working process, circulating water in heat-exchange tubes will absorb the radiant heat of high-temperature phosphoric oxide smog and partly vaporize while flowing upwardly, to form two-phase (gas-liquid) flow. This explains why its density will be continuously reduced with the increment of vapor content. Owing to the lower operating pressure of drum, the pressure head, depending on the density variation of circulating water between downtake and ascending tube bundle, is great enough to provide a driving force of natural circulation in the water cooling system, which is composed of the drum, downtakes, lower manifold, ascending tubes, upper manifold, and collecting tubes.

Not only can the novel phosphorus tower satisfy the requirements of production and quality of highly pure phosphoric acid, but also can reclaim about 65% thermal energy released by the combustion of phosphorus element, which can convert the cooling water in the heat-exchange tube bundle into saturated vapors with 0.8 MPa pressure. On one hand, these high-temperature vapors can be used to melt the solid phosphorus in the steam-heated vessel. On the other hand, they can be provided to other chemical industries. By comparing the conventional process with the improved process, it has been found that about 560 kg standard coal and 400 t circulating water will be saved for every ton of phosphorus combusted, which means the cost reducing by nearly $12 to produce per ton of phosphoric acid at a concentration of 85%.

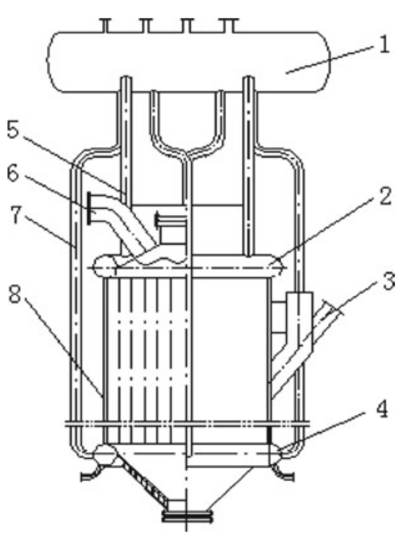

Fig. 1 Structure of novel energy-saving phosphorus tower. 1—drum, 2—upper manifold, 3—burner, 4—lower manifold, 5—collecting tubes, 6—gas/aerosol exit, 7—downtakes, 8—water wall

3. Phenomena and Mechanism of High-Temperature Corrosion

On account of the strong hygroscopicity, phosphoric pentoxide will absorb the moisture in the liquid phosphorus and natural air and turn into phosphoric acid or other phosphoric polymers, which will cause obvious corrosion on the heated metal at high temperature (Ref 3, 4). Therefore, it is most critical to tackle these problems resulting from the corrosive medium when designing the novel phosphorus tower with heat recovery.

By analyzing the results from the experiments in laboratory, pilot-scale single tube tests, and field measurements of industrialized devices, it is concluded that the fins close to the burner of the novel phosphorus tower, the heat-exchange tube facing the flame, and the welds between tubes and fins are more likely to be corroded, which have been proved by the corrosion phenomena of existing industrial phosphorus tower, as shown in Fig. 2 to 4.

Fig. 2 Corrosion of irregular fin near burner

Fig. 3 Corrosion of bent tube near burner

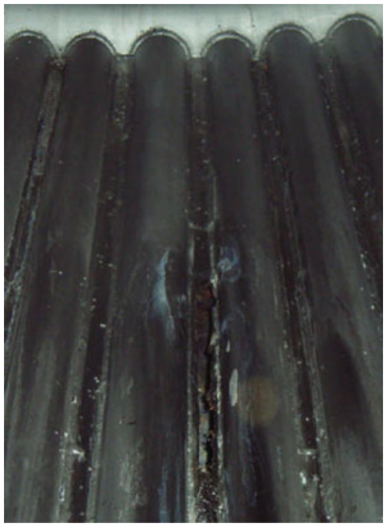

Fig .4 Corrosion of fillet weld between heat exchange tubes and fins

After replacing conventional jacket with membrane water wall, the temperature of the heated metal surface of phosphorus reaction tower will rise from original 50 °C to above saturation temperature corresponding to the pressure of byproduct steam. Usually, the higher the pressure of byproduct steam is, the higher the wall temperature will be. It is necessary to point out that the saturation temperature corresponding to the pressure of byproduct steam is the lowest one of membrane water wall, the highest temperature lies at the center of fins. In particular, the locations adjacent to the burner, for the sake of sufficient space to situate the wind pipe and so on, the heat-exchange tubes are usually bent inwards. Limited to the fabricating process, here the fins become bigger and more irregular, thereby the core temperature of local irregular fin is highest and its corrosion is also most serious (Ref 5–7), which can be seen in Fig. 2. Thus, to avoid the overheating corrosion of membrane water wall, it is of great significance to install effective cooling components on the periphery of phosphorus burner and to determine appropriate pressure of saturated vapor.

Figure 3 shows the corrosion on the heat exchange tubes of novel phosphorus tower. The characteristic of this kind of corrosion is obviously regional and concentrative, only can be observed on the bent tubes near the burner of tower manufactured by particular companies in particular regions. According to the metallographic analysis of failure tubes and component analysis of both corrosion products and cooling medium, it is certain that the damage of tubes is the result of stress corrosion, erosion of high-temperature corrosive medium outside the tubes, and wall-thinned processing. Under the working conditions, each heat exchange tube can be regarded as an internal pressure vessel exerted unequal loads with nonzero axial and circumferential tensile stress. In such a stress state, if water without any treatment is directly used as the cooling medium, stress corrosion can easily occur as an evoking result of tensile stress and chloride ion. Besides, bending process will bring into partial thinned effects on heat exchange tube in some way, and the bent zone of tube becomes the weakest one. Concluded from the above-mentioned factors, the final destruction of membrane water wall appears on the bent tubes near the phosphorus burner. In order to avoid such corrosion, the quality of cooling water should be strictly controlled and the content of chloride ions should be no more than 25 ppm. What is more, the strength weakening effect caused by processing thinning should be taken into consideration to provide enough margins beforehand.

Being the novel phosphorus tower, welds are more vulnerable to high-temperature corrosion. Figure 4 illustrates the appearance of high-temperature corrosion on fillet weld between heat exchange tube and fin in phosphoric acid and its polymers environment, which is concerned with the partial variation of material properties in the welding process (Ref 8). In order to diminish corrosion, current phosphorus reaction towers are made of ultralow carbon stainless steel 316L, whose resistance to phosphate corrosion is attributed to its 17% chromium (Cr) content. Steel's surface will be passivated to form a stable dense oxide layer to separate the metallic matrix from the corrosive medium when its content of chrome element is within 12-17%. However, 316L stainless steel has sensitization in the welded area where the temperature is around 650-700 °C, i.e., carbides ($Cr_{23}C_6$) in stainless steel will precipitate intercrystallinely. As a result of chromium precipitating slower than carbon, the carbon will be gathered quickly in the vicinity of grain boundaries while the chromium will not. As the welding process is going on, the precipitation of carbides continues and finally partial regions of grain boundaries get chromium-deficient. If chromium content is lower than the required limited passivated content (usually higher than 12%), severe corrosion will occur intercrystallinely. For the sensitive zones in the welding process, the fillet welds between heat exchange tubes and fins as well as those between lower manifold and the steel around head come into being intercrystalline corrosion more easily. Thus, to the novel energy-saving phosphorus tower, selecting appropriate electrode and the postweld quick cooling is of great importance to avoid staying too long within sensitizing temperature range. If necessary, integral high tempering is needed to improve the welds' resistance to corrosion.

4. Anticorrosive Measures of Novel Energy-Saving Phosphorus Tower

Corrosion should be paid sufficient attention to the design, manufacture, and operation of novel phosphorus tower, which directly affects the life and operational stability of equipment and even the security and economy of the entire production system. Therefore, based on the full analysis of corrosive mechanism, taking into account of validity and operability, combined with the optimization to design, manufacture, operation, and so on, the goal of full-life anticorrosion to novel phosphorus tower will be achieved.

4.1 Process Anticorrosion

As a sort of complex process equipment, the anticorrosion to the novel phosphorus tower can be realized by reasonable regulation and control of process conditions according to the characteristics of corrosive media. It is suggested that P_2O_5 will absorb the water vapor in air, which contributes to polymeric phosphoric acid in the running process of novel phosphorus tower (shown by Fig. 5). This polymeric acid then will condense on the water wall membrane, forming a barrier layer,

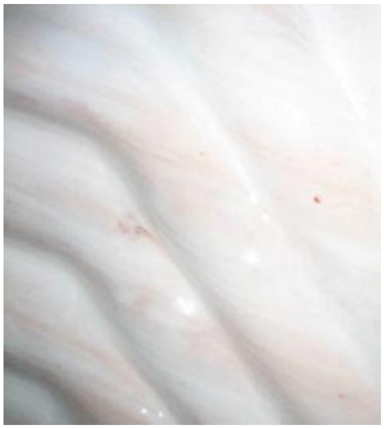

Fig. 5 Deposit attached on membrane water wall

preventing the high-temperature corrosive smog directly contacting with tower wall. Generally, the lower the surface temperature of water wall, the thicker the solid deposit, the stronger the protective effect and the greater the thermal resistance will be. Through analyzing the deposit, it is discovered that the deposit mostly contains the polymer of ultraphosphoric acid, whose coefficient of heat conductivity is 2.06 W/m·K with no fixed melting point and which melts within 490-510 °C, volatilizes at 590 °C and lasts until 633 °C, at this point to volatilize thoroughly. Therefore, to ensure the formation of protective deposit, the surface temperature of membrane water wall should be controlled at a temperature which is 50-100 °C lower than the melting point of deposit. In its practical application, stable operating conditions and narrow fins are recommended, especially effective cooling measures should be adopted to maintain the temperature of water wall subjected to higher heat loads within the range of 390-440 °C.

4.2 Structure Anticorrosion

As the highly dangerous area of corrosion failure, the water wall of oblique burner must be furnished with excellent cooling parts to lower temperature and prevent corrosion, thereby weakening the effect on the waste heat recovery ratio. Heat exchange tubes around oblique burner of the early developed phosphorus tower are usually bent inwards (shown in Fig. 6). However, this method is a two-edged sword; the advantages are the structural integrity and the maximization of waste heat recovery, yet the disadvantages are the process thinning and the over-wide size of irregular fins. In fact, the corrosion has happened in this region, so the local cooling structure has been improved as shown in Fig. 7. For the novel cooling structure, the heat exchange tubes around the phosphorus burner are shortened and local manifold and jacket are added (Ref 9). Evidence indicates that the novel structure is able to cool the heating surface effectively and influence on the waste heat recovery ratio minimally.

4.3 Surface Anticorrosion

When the temperature of membrane water wall is below 490 °C, there will be protective solid deposit attaching on its surface. However, the fluctuations of phosphorus consumption, air flow, and circulating water flow are inevitable in a long, continuous period, and the temperature of water wall will be in dynamic variation correspondingly, even likely to surpass the

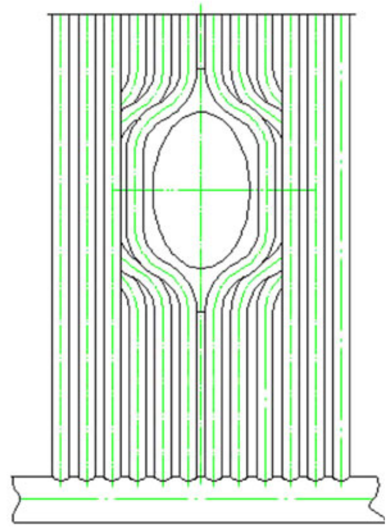

Fig. 6 Layout of heat exchange tubes bent inwards near phosphorus burner

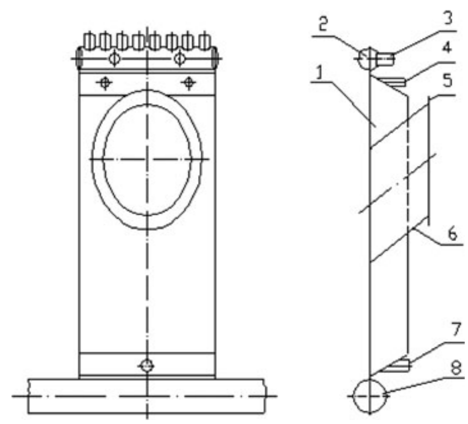

Fig. 7 Local water cooling jacket around burner

allowable temperature range. Therefore, it is favorable to enhance the corrosion resistance of equipment and enlarge the service range of available materials if special corrosion-resistant coating is sprayed on the inner surface of membrane water wall.

Ceramic material has good corrosion resistance to high-temperature phosphoric acid and plasma spraying is a kind of novel surface hardening technology. Consequently, a plasma sprayed ceramic coating becomes a perfect combination of both material and application technology. With the help of corrosion experiments in laboratory, pilot-scale single tube tests and field measurements of industrialized devices, the anticorrosive plasma ceramic coating made up of 0.2 mm NiCrAl bond coating, 0.5 mm ZrO_2 top coating, and silicate sealer are spread onto the inner surface of membrane water wall, which can effectively prevent the corrosion of high-temperature phosphoric acid as well as its polymer and has been applied successfully in industrial units (Ref 10).

4.4 Materials Anticorrosion

At present, phosphorus towers are mostly made of stainless steel, particularly Cr-Ni stainless steel. In the specific selection of stainless steel, the principle should be adhered to enhance the passivity of material. Generally speaking, chromium as the most important element in stainless steel can improve the stability of passivated layer and strengthen the resistance ability to spot corrosion and gap corrosion. Nickel element in stainless steel can help to enable the formation of austenite and to improve the anticorrosion performance and mechanical property, particularly to protect steel from stress corrosion. As another important element, molybdenum has the same functions as chromium. In addition, the lower the carbon content in stainless steel, the stronger the capacity to resist intercrystalline corrosion. Usually the elements of Ti, Co, and Nb are also added to stainless steel to improve its comprehensive properties. Based on the above analysis and the three major corrosion forms of the novel energy-saving phosphorus tower, it is not difficult to figure out that the most appropriate material is the ultralow carbon austenitic stainless steel rich in Cr, Ni, and so on, and 316L (00Cr17Ni14Mo2Ti) used currently is such a material.

Because of the variety of forms and causes of high temperature corrosion behavior in phosphoric acid, the practical anticorrosion must rely on the synergy of multiple measures. In summary, the structure of novel phosphorus tower is able to ensure the effective cooling of each heating surface, special plasma ceramic coating on key positions and zones subjected to higher heat loads is helpful to prevent high-temperature corrosion, selecting suitable material, controlling the consumption, and quality of yellow phosphorus and regulating the flow of air and circulating water is essential as well.

5. Conclusions

Since the energy utilization in conventional production of furnace grade phosphoric acid is rather unreasonable, a novel phosphorus reaction tower with circulating water wall has been developed, which can satisfy the production requirements of phosphoric acid and effectively recover the reaction heat. High-temperature anticorrosion plays a critical role on recycling and utilizing the reaction heat in the production of phosphoric acid, and significantly affects the security and economy of the whole production system.

Furthermore, the type of high-temperature corrosion is diverse as follows:

- the overheating corrosion at the center of the fin close to phosphorus burner,
- the intercrystalline corrosion of the weld between fin and tube,
- the stress corrosion between the bent and the thinned heat exchange tubes.

In order to obtain the life cycle safety, the synergy of multiple measures is necessary to the industrial equipment in continuous service.

It has been proved that:

(1) 390-440 °C surface temperature of water wall;
(2) local water cooling jacket around the oblique burner;
(3) plasma-sprayed ZrO2 ceramic coating on heating surface;
(4) ultralow carbon austenitic stainless steel rich in Cr and Ni elements.

All these are dramatically effective both in reduction of water wall temperature, from 600 °C formerly to 80 °C presently, and in prolonging the lifespan of device in service, from less than 5 years to nearly 8-10 years; In addition, compared with the traditional method, changing dried air into untreated natural air for this new-style tower can increase the waste heat recovery ratio to about 65% and reduce the production cost by over 4.3%, by per ton 85% phosphoric acid.

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