Metal Material Resistant to Hydrochloric Acid Corrosion

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Abstract. Hydrochloric acid, especially when contains a certain amount of FeCl₃ (or oxidizing salt such as copper chloride), is highly corrosive to chemical equipment, which will lead to problems of malignant destruction and failure. Therefore, the correct and rational selection of material is essential for the production and use of hydrochloric acid. In this paper, from the corrosion characteristics of hydrochloric acid and the factors affecting the selection of hydrochloric acid resistant materials, the metal materials resistant to hydrochloric acid corrosion are reviewed, which provides a scientific basis for material selection of alumina extraction from fly ash by acid method and other similar working conditions.

1. Introduction

In recent years, along with the vigorous development of petroleum, chemical, pharmaceutical, clean energy and other industries, the medium environment in which materials and equipment are located is becoming more and more complex, which puts forward higher requirements for the corrosion resistance of engineering materials. In engineering design, it is often the case that hydrochloric acid is present in working conditions. When there are both air and oxidant in the hydrochloric acid medium, the corrosion condition becomes extremely harsh and the corrosion phenomenon is more serious[1, 2]. Especially, hot concentrated hydrochloric acid containing a certain amount of FeCl₃ (or oxidizing salt such as copper chloride) is highly corrosive, which has become a material blank for industrial metals and alloys as well as many non-metallic materials that cannot be filled, that is to say, it is difficult to select economical and durable corrosion-resistant materials[3].

In the current situation of the strategy of promoting clean energy, the extraction of alumina from fly ash of power plants has become a hot spot[4, 5]. Many large enterprises and researchers have invested a lot of energy in this field and made some achievements. Since 2004, Shenhua Zhuneng Resources Comprehensive Development Co., Ltd. has been working on the extraction of alumina by acid method. The process of extracting alumina from fly ash by "one-step acid dissolution method" has been developed independently and successfully, which has a short process, reusable silica slag and other advantages. It is the most efficient and environmentally friendly process of extracting alumina at present, and has great development prospects[6]. The "one-step acid-dissolving" process uses recyclable hydrochloric acid as the reaction medium, and there is an erosion effect of SiO₂ particles during the flow of the medium, so the medium environment is more harsh.

Therefore, from the corrosion characteristics of hydrochloric acid and the factors affecting the selection of hydrochloric acid resistant materials, the metal materials resistant to hydrochloric acid corrosion are emphatically discussed in this paper, so as to provide a scientific basis for the process of extracting alumina from fly ash by hydrochloric acid method and other similar working conditions.
2. Corrosion characteristics of hydrochloric acid

Hydrochloric acid is a typical non-oxidizing strong acid, which can be completely dissociated into $H^+$ and $Cl^-$. Most common metal materials undergo severe activation corrosion in the hydrochloric acid system, and the corrosion rate is remarkable with the increase of concentration and temperature of hydrochloric acid. In addition, in the hydrochloric acid medium, due to the existence of a large amount of highly active chloride ions, it can destroy the passivation film on the surface of the metal material, causing comprehensive corrosion of the material, pitting corrosion and stress corrosion cracking of stainless steel and many other metals [7,8]. Generally speaking, it is more difficult to choose a material resistant to hydrochloric acid than sulfuric acid. Although from the point of view of the corrosion resistance alone, some non-metallic materials have better corrosion resistance than the metal materials in the hydrochloric acid medium, the application of metal materials are much wider because of their mechanical, wear resistance, thermal stability and other comprehensive properties. However, some common metal materials cannot be used due to their poor corrosion resistance. Only a few special metals such as titanium, zirconium and tantalum have a strong passivation tendency and alloys such as nickel-based and molybdenum-based have strong thermodynamic stability, can be used in hydrochloric acid medium [9].

3. Factors affecting the selection of hydrochloric acid resistant materials

In the equipment design of petroleum and chemical industry, it is a very important and complicated problem to select the materials of key equipment reasonably, which is directly related to the performance, service life, safety, economy and reliability of the equipment. Under normal circumstances, the appropriate materials should be selected according to the working conditions (temperature, pressure, stress, wear, special materials, life, etc.) and surrounding environmental conditions (temperature, humidity, pollution, pH, etc.).

The factors affecting the corrosion resistance of metal materials to hydrochloric acid are mainly divided into internal and external factors. The internal cause depends on the selected metal material, and the external cause is mainly the external environment in which the material is located [10]. The corrosion resistance of the metal material itself against hydrochloric acid is the main factor to be considered in material selection. It mainly includes alloying elements and impurities in the material, the surface state of the material, the internal stress of the material and the working conditions of the material. Problems in any of these factors can lead to material failure. For example, the addition of alloying elements with strong corrosion resistance can significantly improve the hydrochloric acid corrosion resistance of the alloy, but this does not necessarily mean that infinite addition can be made. According to Tammann's law, there is a critical value for the amount of alloying elements added, after which the corrosion of the alloys will change dramatically [11]. Therefore, it is necessary to add alloying element in an appropriate amount. Although the key factor determining the corrosion resistance of metal materials to hydrochloric acid is on the metal material itself, the final choice of corrosion resistance to hydrochloric acid materials often depends on the external environment. Such as material physical properties, mechanical properties and manufacturing formability meet the overall requirements of the system equipment, the economics of the material, and the length of the supply cycle.

Of course, the above factors affecting the selection of materials resistant to hydrochloric acid corrosion are independent of each other, and there is a mutual influence and mutual restriction relationship between them. In a word, when selecting metal materials resistant to hydrochloric acid corrosion, we should consider all kinds of influencing factors comprehensively, proceed from system integrity, weigh the advantages and disadvantages of each scheme from the perspective of technology, economy and safety balances, and choose the scheme which is applicable in production, advanced in technology, reasonable in economy, reliable in safety and environmental protection.

4. Metal material resistant to hydrochloric acid corrosion

It can be seen from the above that the selection of hydrochloric acid is a difficult task, which requires comprehensive consideration of a variety of factors. Since different materials will show different corrosion resistance in different environmental media, the choice of hydrochloric
acid-resistant metal materials must first consider the corrosive environment in which the materials are located (such as the concentration of hydrochloric acid, temperature, and other impurities). Schillmoller[12] has systematically studied the hydrochloric acid corrosion resistant materials and drawn the selection diagram of hydrochloric acid resistant materials. Figure 1 shows an equal corrosion line with a corrosion rate of 0.05 mm/year at different hydrochloric acid concentrations and temperatures, which is usually used as a design upper limit for alloy selection. As can be seen from the figure, the concentration-temperature state diagram of hydrochloric acid is divided into five regions, and the materials suitable for the temperature and concentration range in each region are listed in Table 1. It is worth noting that the various metal materials listed in the table are derived from a large number of corrosion test data and the experience of the factory, without taking economic factors into account.

Figure 1 Selection of hydrochloric acid resistant materials
The materials listed in Table 1 are only suitable for the case where the material is in a concentrated hydrochloric acid with a static or low flow rate. If the hydrochloric acid contains other impurities that can significantly change the corrosion characteristics of the material or the high flow rate of acid making the material wear and corrode, the materials listed in Table 1 may not be able to play a role in preventing the corrosion of the material by hydrochloric acid. Moreover, when we select materials, we must also consider the physical properties, mechanical properties, economy, supply cycle, working conditions and other factors of the materials for comprehensive analysis and comparison.

5. Introduction and research progress of common metal materials resistant to hydrochloric acid corrosion

5.1. Nickel and nickel based alloys

Metal nickel has good ductility, medium hardness, and usually belongs to the face-centered cubic unit cell, and the structure is very stable. Nickel has good resistance to erosion of non-oxidizing acid. In addition, nickel is an austenite stabilizing element. The addition of a large amount of nickel can significantly improve the solid solubility of corrosion-resistant alloying elements (such as Cr, Mo, Fe, Cu, etc.), and thus can form a wide variety of alloys. The passivation element added in the nickel-based alloy can improve the corrosion point and thermodynamic stability of the material.
Moreover, the alloying element can also promote the formation of a dense corrosion product protective film on the surface of the alloy, so that the nickel-based alloy has good comprehensive performance and can be resistant to various acid corrosion and stress corrosion[13].

Among nickel-based alloys, Hastelloy alloy is currently recognized as one of the best metal materials to hydrochloric acid corrosion[14]. In order to solve the problem of hydrochloric acid resistance to chemical equipment in the early stage, Hastelloy A alloy (0Ni60Mo20Fe20) was developed, which solved the corrosion problem of hydrochloric acid at 70°C. Later, it was gradually found that the corrosion resistance of nickel alloys in reducing acid medium could be greatly improved by adding a large amount of Mo. Hastelloy B alloy (0Ni65Mo28Fe5) emerged as the times required, and it is the alloy with the strongest corrosion resistance to hydrochloric acid. It shows good corrosion resistance to any concentration of hydrochloric acid below the boiling point. Hastelloy B-2 alloy is a new type of Nickel-Molybdenum Alloy developed on the basis of Hastelloy B. It has excellent corrosion resistance to reducing medium. In hydrochloric acid of 160 °C and 2% concentration, the corrosion rate is less than 0.13-0.51 mm/a. It is commonly used in parts of corrosion-resistant equipment under extremely harsh conditions of hydrochloric acid corrosion[15]. The Hastelloy B-3 alloy is a new Ni-28Mo nickel-based alloy developed in the 1990s. Under the hydrochloric acid system, the corrosion resistance and thermal stability against stress corrosion are improved. In the range of room temperature to boiling point, the corrosion rate of Hastelloy B-3 alloy in concentrated hydrochloric acid and dilute hydrochloric acid with weak oxidation ability is not more than 0.5 mm/a, showing good corrosion resistance. Wen et al.[16] 's study on the hydrochloric acid resistance of Hastelloy B-3 alloy showed that the alloy presented good corrosion resistance in pure hydrochloric acid, but it was not suitable for hydrochloric acid containing oxidizing ions or high dissolved oxygen, because Mo⁴⁺ passivation film would be oxidized into Mo⁶⁺ after the addition of oxidizing ion Fe³⁺, resulting in a sharp decrease in corrosion resistance. Hastelloy C alloy is a Ni-Cr-Mo nickel-based alloy with excellent corrosion resistance in both oxidizing and non-oxidizing acids. The Hastelloy C-276 alloy was developed by controlling the content of carbon (<0.02%) and silicon (<0.08%) based on the Hastelloy C alloy, which is the most resistant of modern metal materials. It has excellent corrosion resistance under oxidizing or reducing conditions and in the presence of halogen ions, and is therefore widely used in harsh corrosive environments[17].

5.2. Zirconium and zirconium alloys

Zirconium is a group IV-B element of the periodic table and belongs to refractory metals. It has many excellent properties such as high melting point, low expansion coefficient, excellent mechanical properties and good corrosion resistance. Zirconium is mainly used in nuclear reactors and chemical equipment. It is very active and can react with the environment at relatively low temperatures. When zirconium is exposed to air during heating, a dense oxide film is formed on its surface, which makes zirconium and its alloys have excellent corrosion resistance. Zirconium and its alloys have strong corrosion resistance to most hydrohalic acids, especially hydrochloric acid, hydrobromic acid, hydroiodic acid and hypochlorous acid[18]. The corrosion rate is less than 0.13mm/a in all concentration hydrochloric acid at atmospheric, boiling point or higher temperatures[19]. However, their expensive price limit their widespread use.

5.3. Tantalum and tantalum alloys

The materials with the best corrosion resistance in hydrochloric acid are tantalum and tantalum alloys, which are completely inert in various concentrations of hydrochloric acid and exhibit excellent corrosion resistance. Therefore, they can be used in the environment of hydrochloric acid for a long time[20]. The special corrosion test data[21] show that the corrosion rate of tantalum is less than 0.025 mm/a in hydrochloric acid with temperature lower than 190°C and concentration below 25%. The very thin, corrosion resistant and stable oxides are formed on the surface of tantalum and its alloys, resulting in outstanding corrosion resistance. However, the cost of tantalum alloys is very expensive, and it is uneconomical to manufacture large-scale equipment.
5.4. Titanium and titanium alloys

Titanium is a very active metal with a low equilibrium potential and a high tendency to thermodynamically corrode in the medium. Pure titanium will cause corrosion in more than 5% hydrochloric acid, but the affinity between titanium and oxygen is very strong. When oxidizing substances are added, such as copper chloride and ferric chloride, a dense and inert oxide film can be formed on the surface of titanium to inhibit the corrosion of titanium. However, the Ti oxide film is susceptible to destabilization in concentrated reducing acids, such as hydrochloric or sulfuric acid, which lead to accelerated mass loss rates. Therefore, alloying additions, which can promote the stability of the protective oxide film in a reducing acidic environment, are desired. The alloying additions of Nb\(^{[22]}\), Zr\(^{[22, 23]}\) and Ni\(^{[24]}\) to Ti can improve the resistance of Ti-based oxides. If trace alloying element Pd (0.1%~0.2%) is added to titanium, the performance of titanium-palladium alloy against hydrochloric acid corrosion will be greatly improved. Studies have shown that the corrosion rate of titanium-palladium alloy in 5% hydrochloric acid at 208\(^\circ\)C is about 0.1 mm / a and at boiling point, the corrosion rate in 5% hydrochloric acid is about 0.05-0.16 mm/a, which is a promising materials resistant to hydrochloric acid corrosion\(^{[25]}\).

5.5. Other metal materials and their research progress

In addition to the above-mentioned metal materials and their alloys, various metal materials resistant to hydrochloric acid corrosion have been explored and studied. The results are as follows:

Kong et al.\(^{[26]}\) invented an alloy resistant to concentrated hydrochloric acid corrosion. The composition of this alloy is Cr22~24%, Mo16~19%, Cu1.3~2.2%, C≤0.02%, at 75 °C. In the case of 75 °C, 17% hydrochloric acid and 1% FeCl\(_3\), the corrosion rate was 0.51 mm/a.

Yin et al.\(^{[27]}\) invented a 3YC21 alloy resistant to hydrochloric acid corrosion. The composition of this alloy is Mo28~30%, V 0.3~0.8%, some rare earth trace elements, C≤0.02. The corrosion rate is ≤0.1mm/a when the concentration of hydrochloric acid is 27~30% and the temperature is 50~70°C, while in the case of room temperature and any concentration of hydrochloric acid, the corrosion rate is <0.031mm / a.

Laboratory studies by Derbyshev et al.\(^{[28]}\) have shown that after the corrosion of a 2% hydrochloric acid solution at 95-100°C for 1000 h, the corrosion rate of VT1-0 titanium alloy, 06KhN28MDT alloy and corrosion-resistant Cr-Ni-Mo steel 10Kh17N13M3T was lower than 0.01 mm/a, which can be used in low hydrochloric acid concentrations. Zirconium and tantalum exhibited strong resistance to uniformity and localized corrosion in a 20% hydrochloric acid solution at 95-100°C. After 1000 h corrosion, the corrosion rates were 0.020 mm /a and 0.001 mm /a, respectively.

Alain Robin et al.\(^{[20]}\) studied the thermal hydrochloric acid resistance of niobium, tantalum and niobium-tantalum alloys (containing 20, 40, 60, 80 wt% tantalum). The results showed that with the increase of tantalum content, the hydrochloric acid corrosion resistance of the alloy was improved, and when the content of tantalum reached 60%, the alloy materials had considerable corrosion resistance.

Researches\(^{[29]}\) have been reported that the corrosion rate of Niobium in concentrated hydrochloric acid at 110°C during 7 days is about 0.1 mm / a. When exposed in concentrated hydrochloric acid, Niobium can be corroded through a competing process involving the oxidation of Nb to Nb\(_2\)O\(_5\) and the chemical dissolution of this oxide to Nb(OH)\(_4\)^+.\(^{[30]}\)

Mishra\(^{[31]}\) et al. Studied the corrosion performance of some commercial nickel-based alloys(such as C-276 (UNS N10276), C-2000 (UNS N06200), C-22 (UNS N06022), Alloy 625 (UNS N06625), Hybrid-BC1 (UNS N10362) and B-3 (UNS N10675)) in HCl solutions, with and without the presence of oxidizing impurities (ferric ions). According to the experiment, The highest corrosion resistance in concentrated HCl solutions is obtained by the additions of high molybdenum content in Ni-based alloys. In the presence of moderate to high levels of oxidizing impurity (Fe\(^{3+}\)), an alloy with a high Cr content (N06200, N06022) is required to maintain a low corrosion rate.
6. Outlook

With the continuous development of petrochemical and other industries, equipment is bound to face higher temperatures, higher concentrations of hydrochloric acid, and more solids in hydrochloric acid. More materials with better performance will be produced to serve in the harsh environment of high temperature, high concentration of hydrochloric acid and high solid content.

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References
[1] Tianhua Chemical Machinery and Automation Research and Design Institute, Corrosion and Protection Handbook: Volume 2 Corrosion Resistant Metal Materials and Corrosion Protection Technology, Chemical Industry Press, Beijing, 2006.
[2] W.D. Callister, W.D.C. Jr, D.G. Rethwisch, Materials Science and Engineering an Introduction. 9th Edition, John Wiley &Sons, Inc. 2013.
[3] S.S. Pei, Metallic materials resistant to hydrochloric acid corrosion, Technology Today (4) (1981) 34-35.
[4] J. Ding, S. Ma, S. Shen, Z. Xie, S. Zheng, Y. Zhang, Research and industrialization progress of recovering alumina from fly ash: A concise review, Waste Management 60 (2016) .
[5] F.W. Zheng, C. Sun, F.J. Chen, L.I. Guo-Bin, S.U. Yi, A review of extracting alumina from fly ash, Modern Chemical Industry (2018).
[6] Y.W. Wang, L.T. Song, Z.H. Guo, A Summary of the Technology of Extracting Alumina from High Aluminum Fly Ash, Coal engineering (4) (2013) 112-113.
[7] R.S. Oguike, Corrosion Studies on Stainless Steel (FE6956) in Hydrochloric Acid Solution, Advances in Materials Physics and Chemistry 04(08) (2014) 153-163.
[8] E. Dinjus, P. Kritzer, N. Boukis, Review of the Corrosion of Nickel-Based Alloys and Stainless Steels in Strongly Oxidizing Pressurized High-Temperature Solutions at Subcritical and Supercritical Temperatures, Corrosion 56(11) (2000) 1093-1104.
[9] I. Materials Technology Institute of the Chemical Process Industries, Materials Selector for Hazardous Chemicals, Vol. 3, Hydrochloric Acid, Hydrogen Chloride and Chlorine, 1999.
[10] H.Y. Wang, W. Wang, Selection of Hydrochloric Acid Resistant Materials in Chemical Equipment Design, Journal of Qinghai Normal University (Natural Science Edition) (1989) 56-60.
[11] D.Y. Zhang, Study on medium temperature resistant dilute sulfuric acid and dilute hydrochloric acid materials, Enterprise Technology Development 31(13) (2012) 100-101.
[12] C.M. Schillmoller, Alloys to resist chlorine, hydrogen chloride and hydrochloric acid, Stratigraphie 87 (1980) 161-162, 164.
[13] P. Kritzer, N. Boukis, E. Dinjus, Transpassive Dissolution of Alloy 625, Chromium, Nickel, and Molybdenum in High-Temperature Solutions Containing Hydrochloric Acid and Oxygen, Corrosion -Houston Tx- 56(3) (2000) 265-272.
[14] M. Schütze, R.B. Rebak, R. Bender, Corrosion Resistance of Nickel and Nickel Alloys Against Acids and Lyes, Blackwell Verlag GmbH (2014) 317-322.
[15] R.C. Yang, F.R. Nie, Characteristics, progress and application of nickel-based corrosion-resistant alloys, Journal of Lanzhou University of Technology 28(4) (2002) 29-33.
[16] D.L. Wen, Corrosion Behavior of Hastelloy B3 Alloy in Hydrochloric Acid, Corrosion and Protection 37(6) (2016) 475-480.
[17] R.P. Yan, Study on Corrosion Behavior of Hastelloy B-3 and C-276 in Hydrochloric Acid, Xi'an University of Architecture and Technology, 2005.
[18] C.H. Liang, Corrosion Resistance of Ti, Zr, Ta, Nb Metals and Their Alloys in Hydrochloric Acid Liaoning Chemical Industry (1993) 18-22.
[19] H. Zhang, F.Q. Chen, Corrosion and Protection of Metals in Hydrogen Chloride, Chlorine and Hydrochloric Acid, Mining and Metallurgical Engineering (4) (1982) 47-51.
[20] A. Robin, J.L. Rosa, Corrosion behavior of niobium, tantalum and their alloys in hot hydrochloric
and phosphoric acid solutions, International Journal of Refractory Metals & Hard Materials 18(1) (2000) 13-21.

[21] S.T. Zhou, Corrosion and Protection of Hydrochloric Acid, Hunan Chemical Industry (1) (1979).

[22] S.Y. Yu, C.W. Brodrick, M.P. Ryan, J.R. Scully, Effects of Nb and Zr Alloying Additions on the Activation Behavior of Ti in Hydrochloric Acid, Journal of the Electrochemical Society 146(12) (1999) 4429-4438.

[23] V.V. Andreeva, A.I. Glukhova, Corrosion and electrochemical properties of zirconium, titanium and titanium-zirconium alloys in solutions of hydrochloric acid and of hydrochloric acid with oxidising agents, Journal of Chemical Technology & Biotechnology 11(10) (2010) 390-397.

[24] D. Starosvetsky, J. Yahalom, O. Khaselev, Corrosion Behavior of Heat-Treated Intermetallic Titanium-Nickel in Hydrochloric Acid Solutions, Corrosion -Houston Tx- 54(7) (1998) 524-530.

[25] R.F. Sandenbergh, E. Van der Lingen, The use of Tafel back extrapolation to clarify the influence of ruthenium and palladium alloying on the corrosion behaviour of titanium in concentrated hydrochloric acid, Corrosion Science 47(12) (2005) 3300-3311.

[26] F.Y. Kong, K. Yang, An alloy resistant to concentrated hydrochloric acid corrosion, 2000.

[27] X.Y. YIN, H.Y. WU, Development of 3YC21 alloy for hydrochloric acid corrosion resistance, Functional Materials (3) (1982) 69.

[28] A.S. Derbyshev, A.N. Suriev, A.N. Efimov, I.A. Beresneva, F.A. Ladygin, Corrosion of materials in hydrochloric acid solutions, Chemical & Petroleum Engineering 47(9-10) (2012) 632-634.

[29] D.F. Taylor, Acid Corrosion Resistance of Tantalum, Columbium, Zirconium, and Titanium, Industrial & Engineering Chemistry 42(4) (1950) 639-639.

[30] E. Asselin, T.M. Ahmed, A. Alfantazi, Corrosion of niobium in sulphuric and hydrochloric acid solutions at 75 and 95°C, Corrosion Science 49(2) (2007) 694-710.

[31] A.K. Mishra, N. Ebrahimi, D.W. Shoesmith, P.E. Manning, Materials Selection for Use in Hydrochloric Acid, NACE International, 2016.