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Study on Corrosion Law of Large Crude Oil Storage Tank Floor and Risk-Based Inspection and Maintenance Technology

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In this paper, the author's team has carried out a comparative experimental study on the corrosion characteristics of Q235 steel commonly used in large-scale storage tanks under the specific bottom water environment found with Russian and Daqing crude oil. It was found that there is a certain degree of uniform or local corrosion on the tank floor depending on the kind of bottom water. The bottom water corrosion of Daqing crude oil is a uniform corrosion caused by carbon dioxide. While the Russian crude oil bottom water corrosion is clearly local corrosion caused by co-corrosion of carbon dioxide and hydrogen sulfide, here the corrosion rate is obviously higher than that caused by Daqing crude oil. There are two modes of storage tank inspection and maintenance that have been currently adopted by Chinese refining and chemical enterprises: a regular inspection mode and a API581-2016 risk-based detection mode. These modes have been effectively combined to form an intelligent tank inspection and maintenance mode, software tools to support this intelligent inspection and maintenance management have been developed.

Keywords: *Large crude oil storage tank, Corrosion, Inspection and maintenance, Information system*

1. Introduction

The normal pressure vertical crude oil storage tank has been used as the main storage facility for crude oil, and widely used in oilfield, storage and transportation, oil refining, chemical and other industries. With the continuous expansion of demand for petroleum products in China, the use of large crude oil storage tanks of enterprises has increased significantly. Due to the flammable, explosive, environmentally polluting and toxic characteristics of the medium, the storage tanks are prone to leak, which may lead to major fire and explosion accidents and cause serious casualties, economic losses and environmental pollution. In recent years, China oriental chemical plant "6.27", Huangdao Oil Depot "8.12", Dalian Petrochemical Company "8.29", Shandong Shida Technology Company "7.16" and other accidents indicate that China's oil storage tank accidents are still in a state of multiple occurrences. How to apply scientific risk assessment techniques and reasonable inspection and maintenance strategies to reduce the probability of large crude oil storage tank accidents is still the key.

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2. The main failure mechanism of crude oil storage tank body

The failure mechanisms of crude oil storage tanks are different due to different design and production levels, operating conditions, medium conditions, external environments, inspection and maintenance conditions. The main failure mechanisms of the tank body can be roughly divided into the following four categories without considering the operation reasons and the failure of the attachments:

2.1 Corrosion thinning

According to the corrosion form, it can be divided into uniform corrosion and local corrosion. According to the corrosion site, it can be divided into external corrosion and internal corrosion. External corrosion is mainly due to atmospheric corrosion (especially industrial atmosphere and ocean atmosphere) and soil corrosion (including crevice corrosion in the storage tank floor). The internal corrosion mainly includes the electrochemical corrosion caused by the combination of the H_2S volatilized in the oil, the

CO_2 entering the tank through the breathing valve and the condensed water at the top of the tank, the oil-water interface and the gas-liquid interface corrosion at the tank wall, and the tank bottom corrosions caused by S^{2-}, Cl^-, CO_3^{2-}, etc. contained in crude oil sedimentation water, sulfate reducing bacteria and scaling [1].

2.2 Stress corrosion cracking

Stress corrosion cracking occurs when there is a certain stress in the manufacture and operation of the tank, and the corrosive environment contains the mediums causing stress corrosion. For example, it would occur in the storage tanks in the wet hydrogen sulfide environment and the austenitic stainless steel storage tanks in the chloride ion environment, etc.

2.3 Fatigue fracture

Fatigue mainly includes thermal fatigue and mechanical fatigue. Under the action of external periodic cold and heat and mechanical stress, the storage tank steel will experience fatigue fracture. The fatigue effect of crude oil storage tanks is mainly represented by mechanical fatigue. Mechanical fatigue occurs due to the frequent feeding and discharge of production, which results in alternating loads, and some initial defects such as micro-cracks and weld defects in the equipment itself.

2.4 External natural forces

Factors such as geological disasters, windstorms, floods, earthquakes, and ground subsidence from outside can cause tank failure. For example, the typhoon in the southeastern coastal areas of China, the earthquake disasters in the southwestern seismic belt, and the debris flow in the hilly areas of the mountains are all the main external forces that harm the storage tanks.

In general, the main reason for the failure of the tank body is the corrosion damage [2]. In addition, in recent years, China's crude oil imports have been increasing, and the sources of imports are diversified. The corrosion problems caused by high-sulfur, high-acid and high-salt crude oil to China's crude oil storage tanks are becoming more and more prominent, and it is also a key factor for tank risk assessment.

3. Experimental study on the corrosion law of crude oil storage tank floor in the storage mediums

The author selected the storage tanks for storing two representative crude oils in the storage and transportation workshop of a petrochemical enterprise in Northeast China as the research object, and studied the corrosion law of the tank bottom plate. The storage mediums were Daqing crude oil and Russian crude oil. Two types of tank bottom water were collected as corrosive media to study the corrosion behavior of common storage tank steel Q235 in these two media.

Firstly, two samples of each 1000 ml of the bottom water obtained from the water cut operation of 40,000 cubic meters of crude oil storage tanks in the storage and transportation workshop were collected for component analysis. The two water samples are shown in Table 1 below:

It can be seen that the salinity of the bottom water of Daqing oil tank is significantly larger than that of Russian oil tank bottom, but the S^{2-} content of Russian oil is higher.

The composition of the selected Q235 steel is shown in Table 2 below:

The bottom waters of both of the two storage tanks were collected 20L each, and poured into the experimental device to carry out corrosion coupons and electrochemical experiments. The electrochemical working electrode was made of 1 cm × 1 cm × 0.3 cm Q235 steel sheet (exposed area was 1 cm^2). The copper wire was welded and sealed

Table 1 The bottom water component of Daqing and Russian crude oil storage tank

Composition / Samples	pH	Conductivity	SO_4^{2-}	Cl^-	CO_3^{2-}	HCO_3^-	Mg^{2-}	Ca^{2-}	S^{2-}	Fe^{2-}	Total Salt
		μS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Daqing	8.2	1.22×10^4	33.8	2.39×10^3	132	1.32×10^3	3.12	612	1.83	0.37	6.94×10^3
Russian	8.8	3.68×10^4	36.1	489	117	372	1.92	87.2	3.38	0.12	1.19×10^3

Table 2 The composition of steel Q235

C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	Ni (%)	Cu (%)
0.22	0.35	1.40	0.05	0.05	0.30	0.30	0.30

with epoxy resin. The surface was also passed by 320 mesh, 600 mesh, 800 mesh, 1000 mesh and 1200 mesh sandpaper, wiped with distilled water, absolute ethanol (analytical grade), acetone (analytical grade), and placed in a drying dish for 24 hours. The electrochemical test instrument was an IM6 electrochemical workstation, which was a three-electrode system, the auxiliary electrode was a platinum black electrode, and the reference electrode was an Ag-AgCl electrode. The polarization curve and the AC impedance test were carried out 1 hour after the working electrode immersed in the solution, and the AC impedance spectrum was measured again after 48 hours.

The polarization curve test conditions were as follows: the scanning range was a relative electrode potential of +250 mV to -250 mV and the scanning speed was 5 mV/s. The results are shown in Fig. 1, Fig. 2 and Table 3.

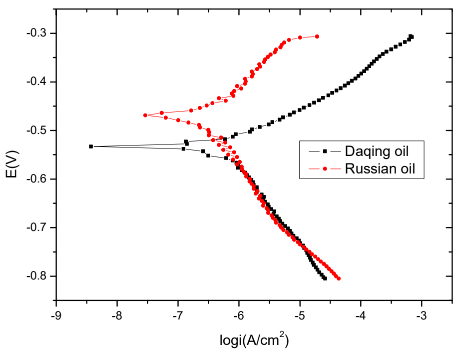
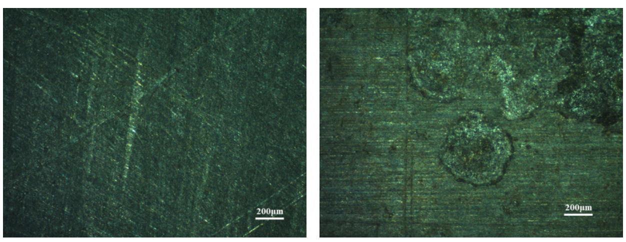


Fig. 1 The polarization curve.



(a) (b)

Fig. 2 Micrograph of piece has immersed in bottom water for a month (×100); (a) Daqing crude oil and (b) Russian crude oil.

Table 3 The results of the polarization curve

Samples	Ecorr (V vs Ag/AgCl)	icorr ($\mu A \cdot cm^{-2}$)	Corrosion ratev (mm/y)
Daqing	-0.533	2.9	0.03
Russian	-0.469	6.1	0.07

It can be seen from the polarization curve that the corrosion reaction of Russian oil is controlled by cathode and anode mixing, and the corrosion reaction of bottom water of Daqing crude oil is cathode control. Although the corrosion tendency of Daqing crude oil bottom water is greater than that of Russian oil from the electrode potential. Although the corrosion tendency of Daqing crude oil bottom water is greater than that of Russian oil from the electrode potential, the ferrous sulfide film of Russian oil formed by corrosion is incomplete and easy to rupture and fall off, which may lead to local corrosion, resulting in more corrosive bottom water of Russian oil. All these indicates that local corrosion of the bottom water of long-term static sulfur-containing crude oil tank should be focused on.

The AC impedance test conditions are: AC amplitude is ±10mV, frequency range is 10KHZ-100KHZ-10MHZ, test results are shown in Fig. 3, impedance equivalent circuit is shown in Fig. 4, R1 is the solution resistance, and CPE1 is the double electrical layer of steel surface and

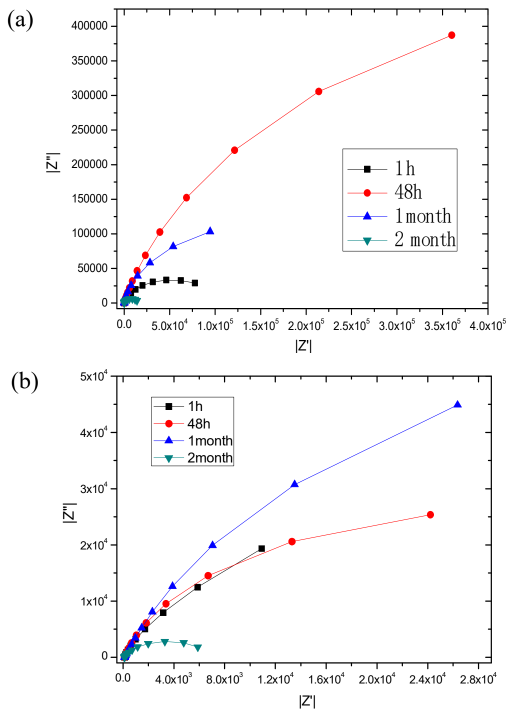


Fig. 3 Nyqusit diagram of AC impedance of test pieces; (a) Daqing crude oil and (b) Russian crude oil.

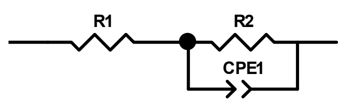


Fig. 4 AC impedance equivalent circuit.

Table 4 AC impedance spectrum fitting parameters

Test pieces	R1(Ω)	R2(Ω)	CPE-T(F)	CPE-P
Daqing 1h	38.15	84603	3.7763E-5	0.86362
Daqing 48h	39.71	974480	1.2678E-7	0.85224
Daqing 1 month	40.11	258320	6.2059E-5	0.88192
Daqing 2 months	37.58	14761	2.3088E-4	0.91221
Russian 1h	107.4	59703	0.00048	0.8838
Russian 48h	114	69706	0.00025	0.86892
Russian 1 month	108.5	200940	1.8743E-4	0.84527
Russian 2 months	98.71	7534	6.5322E-4	0.8202

solution, which is a constant phase angle element; R2 is a polarization resistance, and the parameters of the equivalent circuit are shown in Table 4.

According to the Nyqusit diagram of the AC impedance, the impedance spectrum in the corrosion process always exhibits a typical single capacitive anti-arc semicircle, which is capacitive resistant. It indicates that as the immersion time is extended, the radius of the capacitive anti-arc is gradually increased first and then decreased. It indicates that the corrosion product film formed shows a certain hindrance to the corrosion process at the beginning of the corrosion process. However, as the corrosion film is further thickened, cracking and spalling, resulting in a decrease in the capacitive reactance arc and an increase in the corrosion rate.

Two sets of corrosion hanging pieces were used, 10 cm × 6 cm × 0.4 cm (with an exposed area of 127 cm^2), shown in Fig. 5. The test pieces were polished to 600 mesh, washed with distilled water, wiped with absolute ethanol and acetone, placed in a drying dish for 24 h then weighed. The method shown in Fig. 5 was used to carry out the hanging-piece process: sealed the contact part of the Teflon rod with the test piece with epoxy resin, immersed it in the bottom water of the storage tank and let it stand for 1 month, then took it out and removed the Teflon rod. After mechanically and acetone soaking to remove the epoxy resin, the surface was rinsed with distilled water and wiped with absolute ethanol and acetone. Then the hanging pieces were immersed in 10% HCl + 3% ruthenium (after stirring for 10 minutes, filter out the clear liquid) for 5 minutes to remove the corrosion product and rinsed with the distilled water again. The surface was wiped with absolute ethanol and acetone, and then placed in a drying dish for 24 hours and weighed (balance accuracy: 0.1 mg).

Fig. 4 shows that the bottom water of Daqing crude oil and Russian crude oil has a certain degree of uniform corrosion and local corrosion tendency to the storage tank. However, in the long-term static solution, the corrosion of the bottom water of Daqing crude oil tank is generally uniform corrosion, while the Russian crude oil has obvious local corrosion phenomenon. The corrosion rate of Daqing crude oil tank bottom water is 0.0053 mm/a, and that of Russian crude oil is 0.0102 mm/a, shown in Table 5.

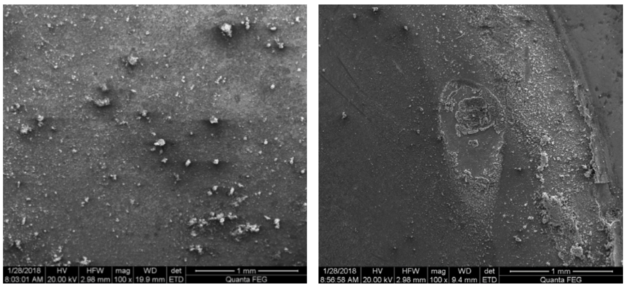
Scanning electron microscopy was used to observe the corrosion hanging pieces after immersion for 1 month. As shown in Fig. 6, it can be seen that the surface of carbon steel is covered by many small massive sediments, and the sediments are scattered on the surface of the car-

(a) (b) (c)

Fig. 5 Schematic diagram of the hanging pieces and the hanging pieces after immersing in bottom water for 1 month; (a) Schematic diagram, (b) Daqing crude oil and (c) Russian crude oil.

Table 5 Loss of corrosion after immersion in Daqing oil and Russian oil bottom water for 1 month

No.	Corrosion area (cm^2)	Loss (mg)	Corrosion rate (mm/y)
Daqing 1	125.92	44.9	0.0055
Daqing 2	127.79	41.3	0.0050
Russian 3	127.42	84.6	0.0103
Russian 4	126.81	82.6	0.0101



(a) (b)

Fig. 6 SEM images of hanging pieces after immersing in bottom water for 1 month; (a) Daqing crude oil and (b) Russian crude oil.

bon steel matrix. The bare carbon steel matrixes are visible between the sediment voids. Compared with that of the bottom water of Daqing crude oil, part of the surface of the hanging piece of Russian crude oil bottom water is distributed with flaky corrosion products.

The EDS analysis of the corrosion products of the hanging pieces of Daqing crude oil and Russian crude oil bottom water is shown in Fig. 7 and Fig. 8. It can be seen that the corrosion products of Q235 carbon steel in Daqing crude oil bottom water mainly contain C, O, Fe and Si, and a small amount of Cl, Mg, Na, S ions, the deposition product is mainly $FeCO_3$. The corrosion products of Q235 carbon steel in Russian crude oil bottom water mainly contain C, S, O, Fe, and there are also a small amount of Cl, Mg, Na, Si and other ions. The deposition products are mainly ferrous sulfide and $FeCO_3$. Comparing the corrosion product components, it can be seen that the reactions in the anode region are all as follows:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The cathodic reaction in the bottom water of Daqing crude oil is mainly as follows:

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

(a)
(b)

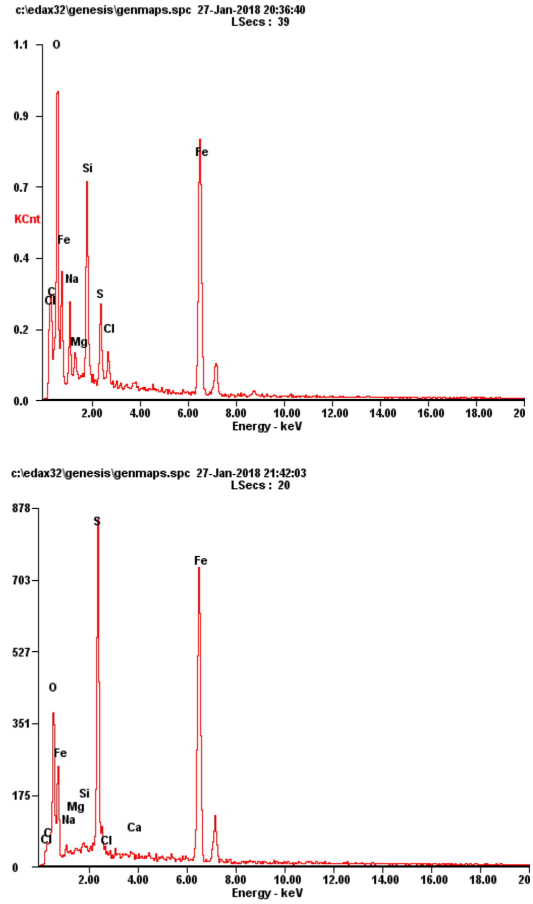


Fig. 7 EDS analysis of corrosion products of hanging piece of crude oil bottom water; (a) Daqing crude oil and (b) Russian crude oil.

(a)

Element	Wt%	At%
CK	22.37	39.87
OK	24.09	32.24
NaK	04.66	04.34
MgK	01.67	01.47
SiK	07.69	05.86
SK	02.84	01.90
ClK	01.21	00.73
FeK	35.47	13.60
Matrix	Correction	ZAF

(b)

Element	Wt%	At%
CK	07.79	19.94
OK	15.73	30.22
NaK	01.22	01.63
MgK	00.00	00.00
SiK	00.38	00.42
SK	15.91	15.25
ClK	00.15	00.13
CaK	00.31	00.24
FeK	58.50	32.19
Matrix	Correction	ZAF

Fig. 8 Composition of corrosion products of hanging pieces of Daqing and Russian oil bottom water; (a) Daqing crude oil and (b) Russian crude oil.

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$
$$2H^+ + 2e^- \rightarrow H_2\uparrow$$

The overall reaction is:

$$H_2CO_3 + Fe \rightarrow FeCO_3 + H_2\uparrow$$

The bottom water of Daqing crude oil is mainly CO_2 corrosion, and $FeCO_3$ is formed to cover the surface of the carbon steel substrate;

There is a certain concentration of H_2S in the Russian oil bottom water, so that in addition to CO_2 corrosion, the cathode reaction also has a reaction as follows:

$$H_2S \rightarrow H^+ + HS^-$$
$$HS^- \rightarrow H^+ + S^-$$
$$2H^+ + 2e^- \rightarrow H^2$$

The overall reaction is:

$$Fe + (1+x)S^{2-} = FeS_{1+x} + 2(1+x)e^-$$

4. Application of risk-based inspection and maintenance technology for storage tanks

At present, there are mainly two types of inspection and maintenance modes for storage tanks in China's petrochemical industry, that are regular inspection and maintenance and risk-based inspection and maintenance (RBI), all of which are operated in a single mode. On the one hand, all enterprises in China's petrochemical industry are subject to the restrictions of Chinese standards and regulations. On the one hand, they are prone to continue the past management mode. Most of them adopt the regular inspection and maintenance mode. That is, according to the standard requirements and combined with the past work experiences, they establish a relatively fixed inspection and shutdown schedule for each component of the tank. The shutdown maintenance period is 3 to 10 years. Petrochemical companies in developed countries in the West have chosen to use risk-based inspection and maintenance methods (RBI) to evaluate tanks and develop effective inspection and maintenance methods to reduce the risk of tanks to ensure the tanks' normal work. In the past ten years, with the promotion and application of risk-based in the petroleum and petrochemical industry, the American Petroleum Institute has continuously updated the API 581 standard based on the summary of the application experiences and research results, and published the first and second edition in 2000 and 2008 respectively. The latest API 581-2016 (third edition) was released in 2016, and the calculation of damage factors and failure consequences in API 581-2016 has also undergone major changes [3].

Relatively speaking, the scientific nature of regular inspection and maintenance mode is insufficient, and the inspection resources are evenly distributed. On the one hand, it takes a lot of human and financial resources to carry out inspections on 80% of low- and medium-risk storage tanks. Sometimes it even demand to stop the production of the entire tank area and open the cans one by one, resulting in invalid use of resources. On the other hand, for 20% of medium- or high-risk storage tanks, it is often impossible to determine the possible failure of the inspection due to insufficient inspection resources, so as to be difficult to effectively control the risk of the tank area. It is no doubt that the RBI inspection and maintenance method can estimate the risk situation of each tank, and can re-evaluate and estimate the approximate time of the next arrival of the risk target after this inspection and maintenance. However, due to the increasingly diversified sources of crude oil sources in China, the storage medium changes frequently. It is necessary to re-evaluate the risk after each medium change, and the assessment workload is large. Otherwise, the risk status of the storage tank between the two assessments will not be grasped in real time, which would make the risk assessment deviate from the actual situation and even lead to an accident.

China's petroleum and petrochemical enterprises began to promote the application of RBI technology in 2003. According to incomplete statistics, about 1600 petrochemical plants of various enterprises have undergone RBI evaluation, which basically covers all refinery devices, chemical plants, storage and transportation, public works and other supporting devices. Moreover corresponding standards and regulations such as GB/T 26610 "Guideline for implementation of risk-based inspection of pressure equipment system", GB/T 30578 "Risk-Based inspection and evaluation for atmospheric pressure storage tanks", SY/T 6653-2013 "Recommended practice for risk-based inspection" and etc. have been formed. However, due to the long-term inherent management mode of the company, coupled with the cumbersome risk assessment procedures for hazardous chemical storage facilities, the poor correlation between the risk assessment and the development and implementation of the maintenance plan, the application of risk assessment results in the enterprise management process is obviously insufficient.

Therefore, in order to effectively solve the problem of the promotion and application of RBI technology in various petroleum and petrochemical enterprises in China, it is necessary to combine the regular inspection and maintenance technology with the risk-based inspection and maintenance technology on the basis of fully considering the risk management of storage tanks, assessing the efficiency of work and the management habits of enterprises. The RBI inspection and maintenance technology is taken as the main management mode, supplemented by regular

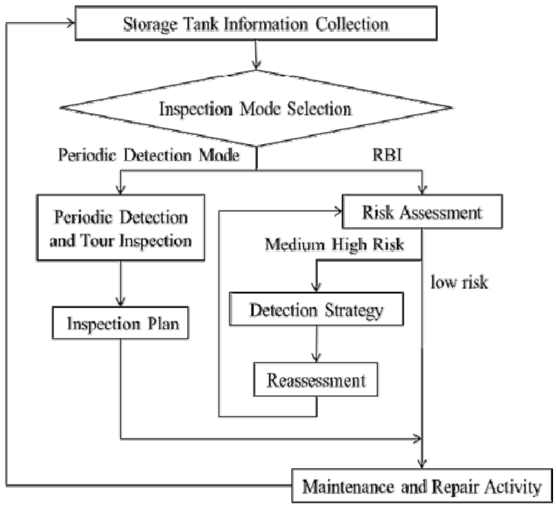


Fig. 9 Principle of tank intelligent inspection and maintenance technology.

inspection and maintenance activities. On the one hand, the results of risk assessment can be applied to guide the focus of regular inspection and maintenance activities. On the other hand, when the medium conditions or operating conditions has changed, the enterprise can refer to the regular inspection and maintenance work to determine whether a tank risk analysis is required. The author team have developed two software systems, China Petroleum Tank Inspection and Maintenance System and Hazardous Chemical Tank Risk Assessment Information System, which enable the tank information to be shared in two inspection and maintenance modes, and establish the intelligence information mode. The mode operation principle is shown in Fig. 9.

China's crude oil storage tank management companies usually carry out inspection and maintenance based on SY/T 5921—2011 "Code of practice for operating, maintenance and repair of vertical cylindrical welded steel oil tank". Based on the current status, the author team have developed the "China Petroleum Storage Tank Inspection and Maintenance System" to standardize the regular inspection and maintenance activities of the enterprise storage tanks. The system is mainly composed of 4 parts, which are storage tank information collection, regular inspection and maintenance inspection, inspection plan formulation and inspection plan implementation. It adopts the back-end language C#, mvc4.5, and the front-end language angular1 for programming development. The system is a web version, no need to install and can be used

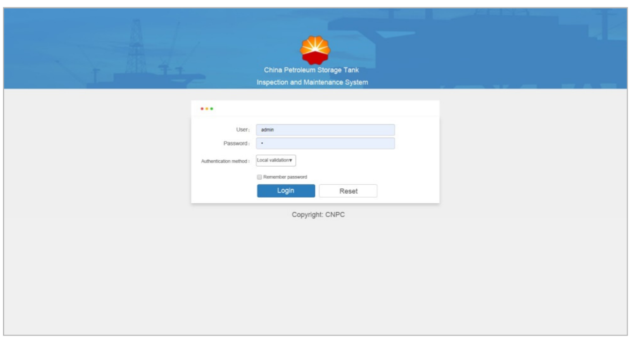


Fig. 10 The login page of China Petroleum Tank Inspection and Maintenance System.

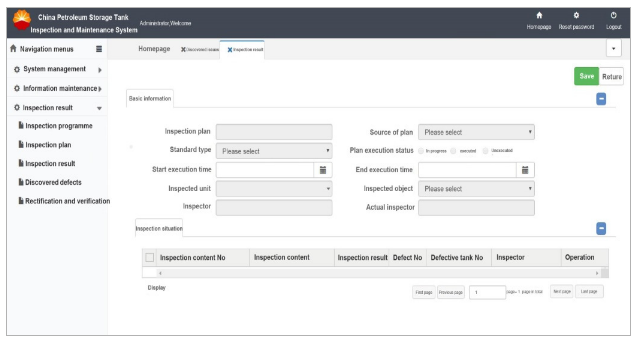


Fig. 12 Tank inspection execution result entry page.

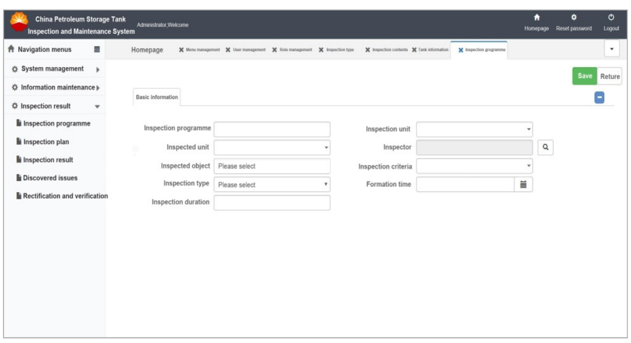


Fig. 11 Tank Inspection Plan Development Page.

Fig. 13 Tank Inspection Finding Problem Statistics Analysis Page.

only by login to the internal network. It becomes an execution module based on risk detection through interface with the risk assessment information system, and provides basic data for further risk assessment of the enterprise. The system interface is shown in Fig. 10 - 13.

Referring to Chinese and international standards such as API 581-2016, API580-2016, API 653-2009, QSY 1362-2011 “Specification for process hazards analysis management”, the author team have developed the Hazardous Chemical Tank Risk Assessment Information System to determine the failure mode of the large crude oil tank area, to carry out comprehensive risk assessment of the tank, to form the risk reduction inspection decision. At the same time they have realized the interface between the two systems, facilitate the application of the results of the tank risk assessment, and provide basic data accumulation for further intelligent inspection and maintenance of demonstration tank areas.

The web version of the Hazardous Chemical Tank Risk Assessment Information System is developed by JavaScript and C#, which is mainly composed of basic information, failure probability, failure consequence, risk analysis, risk matrix, inspection and maintenance, system managementand etc., as shown in Fig. 14 - 18.

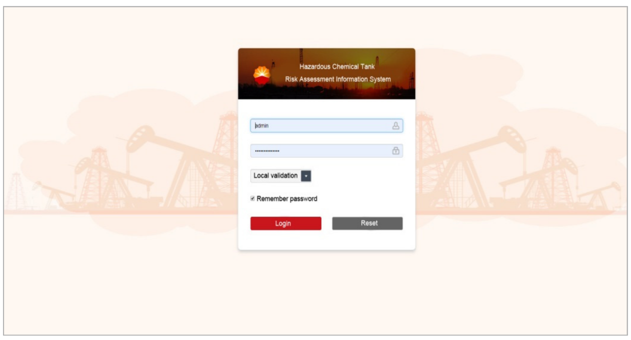


Fig. 14 Risk Assessment Information System Login Page.

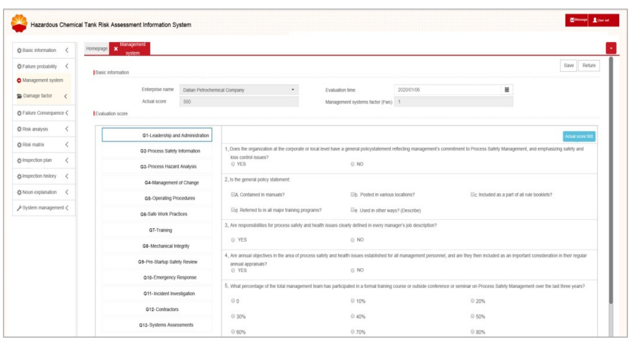


Fig. 15 Tank Management Coefficient Score Page.

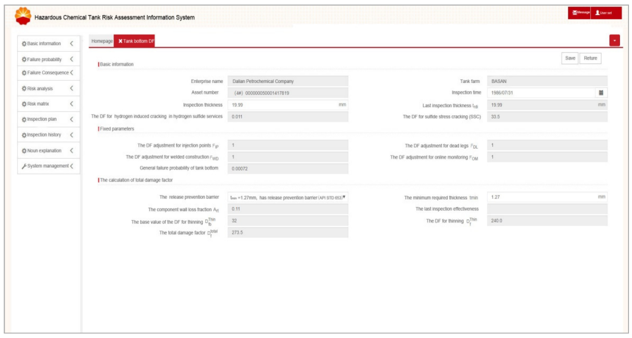


Fig. 16 Tank bottom damage factor calculation page.

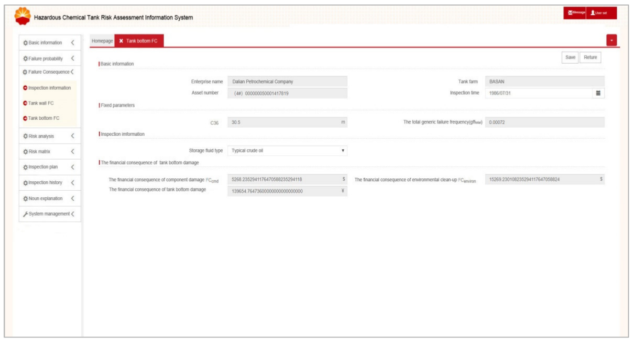


Fig. 17 Calculation page of the financial consequence of the tank bottom.

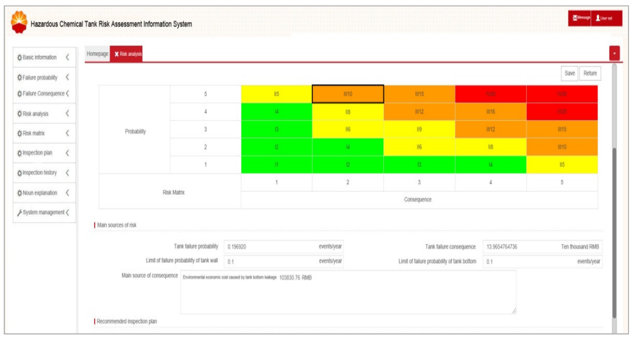


Fig. 18 Tank Risk Analysis Page.

5. Conclusions

The corrosion experiment of the bottom water of Daqing crude oil and Russian crude oil shows that both Daqing crude oil and Russian crude oil bottom water have certain uniform corrosion and local corrosion to the storage tank. The bottom water of Daqing crude oil mainly has uniform corrosion, mainly CO_2 corrosion. Russian crude oil bottom water shows more obvious local corrosion, in addition to CO_2 corrosion there is also H_2S corrosion, and the corrosion rate is significantly greater than Daqing crude oil bottom water.

The inspection and maintenance of oil storage tanks in China's petrochemical industry takes mainly a regular inspection and maintenance mode. At present, RBI technology has been promoted and applied. However, due to the long-term inherent management mode of the company, coupled with the cumbersome risk assessment procedures for hazardous chemical storage facilities, the poor correlation between the risk assessment and the development and implementation of the maintenance plan, the application of risk assessment results in the enterprise management process is obviously insufficient.

In the paper, the intelligent inspection and maintenance information model of the storage tank combine the regular inspection and maintenance technology with the risk-based inspection and maintenance technology on the basis of fully considering the risk management of storage tanks, assessing the efficiency of work and the management habits of enterprises. The RBI inspection and maintenance technology is taken as the main management mode, supplemented by regular inspection and maintenance activities, which is good for Chinese petrochemical enterprises to solve the practical problems of the promotion and application of RBI technology of oil storage tanks.

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