



## Corrosion inhibitor for high temperature oil well

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### ABSTRACT

Serious corrosion is often seen in high temperature oil well which affects its production heavily. On the basis of analyzing the corrosion reason and orthogonal array test, one corrosion inhibitor, HZG, is developed. HZG is aimed to deal with corrosion of high temperature oil well (>100°C). The main constituents of HZG include imidazoline derivative, organic amine and fluor-carbon-imidazoline, which has good corrosion resistant capability, its average corrosion resistant percent is 90% and average corrosion resistant percent on field application is 82%. Field application shows that the HZG can solves most oil wells's corrosion problems and has good corrosion resistant effect.

**Key words:** oil well, corrosion, corrosion inhibitor mechanism, corrosion inhibition effect, orthogonal array test

### INTRODUCTION

Most wells of south Huabei oil field is about 3000 meters deep and the reservoir's temperature is 120°C more or less. High water cut of reservoir (>90%) leads to the serious corrosion of wells. Field application analysis shows that the difference of produced water salinity of this block is remarkably, which is from 5800 mg/L to 16000 mg/L. The main water types are sodium bicarbonate and calcium chloride, corrosion and scale deposit often happen at 800~2000 meters deep, which has the characteristic of pitting corrosion. Frequent pump inspection affect the well production, so chemical anti-corrosion measure is needed to take. The temperature tolerance of conventional corrosion inhibitor for oil well is below 80°C, which can't meet the need of high temperature oil well (>100°C). Corrosion inhibitor, HZG, which has fine temperature tolerance (>130°C), and it has achieved great success on field application.

### EXPERIMENTAL SECTION

Water analysis is carried out on the basis of SY/T5523-2000 *Field Water Analysis Method* and SY/T5329-94 *Clastic Reservoir Flood Water Quality Recommendation and Analysis Method*. The result of water analysis is showed in Table.1. Field corrosion product analysis is shown in Table.2.

Low PH, high salinity, unbounded CO<sub>2</sub> and so on, as is shown in Table.1, 2 were the main reasons of oil well corrosion. Distinct value of the above influential factor will have various corrosion level.[2] One oil well needs one formula.

**Table.1: Produced Water Analysis of Some Oil Well**

sample site	Y9-24x	Y60-81x	Y63-69x	Y60-41x	Y60-8x	Y63-84x	
salinity, mg/L	15377.31	15341.59	8445.76	15612.97	5895.98	7510.14	
Cl <sup>-</sup> , mg/L	8329.95	8675.24	3841.27	8761.56	2287.50	3409.67	
HCO <sub>3</sub> <sup>-</sup> , mg/L	1078.41	827.61	1429.52	940.47	1429.52	1316.66	
CO <sub>3</sub> <sup>2-</sup> , mg/L	0.00	0.00	0.00	0.00	86.32	61.66	
Mg <sup>2+</sup> , mg/L	15.19	18.54	15.19	31.91	12.16	22.79	
Ca <sup>2+</sup> , mg/L	445.89	561.12	55.11	658.82	50.10	62.63	
SO <sub>4</sub> <sup>2-</sup> , mg/L	162.10	0.00	112.87	0.00	60.04	30.02	
Na <sup>+</sup> , mg/L	5345.76	5259.09	2991.79	5220.22	1970.35	2606.72	
CO <sub>2</sub> , mg/L	120.23	18.22	29.15	61.93	0.00	0.00	
water type	calcium chloride	calcium chloride	sodium bicarbonate	calcium chloride	sodium bicarbonate	sodium bicarbonate	
total iron, mg/L	17.30	6.08	3.90	21.60	1.38	0.45	
ferrous iron, mg/L	16.10	3.90	3.25	17.70	0.30	0.10	
sulfur content, mg/L	0.00	0.05	0.00	0.00	1.80	0.00	
pH	indicator paper	6.0	6.5	6.0	6.0	7.0	6.0

**Table.2: Corrosion Product Analysis of Some Oil Well**

well No.	qualitative analysis	quantitative analysis
Y60-81	Visual inspection: black, more hard, react with HCL acutely, abundant air bubble is generated, with foul odor, the corrosion product is dissolved completely, carbonate and sulphide were in it.	Ca <sup>2+</sup> : 3.3%; Fe <sup>3+</sup> : 23.9%; Fe <sup>2+</sup> : 14.3%; igniting decrement: 25.8% acid indissoluble content: 0.28%

## 2.1. Laboratory Formula Experiment

Urotropine(1#), Gemini quaternary ammonium(2#), asphalt imidazoline(3#), amino-ethyl-imidazoline(4#), formaldehyde(5#), thiourea(6#), dodecyl-dimethyl-ammonium chloride(7#) were selected preliminarily and combined with each other on the basis of synergetic corrosion resistant effect. Then concentration, temperature and suitability test were carried on to develop high efficiency and environment friendly formulation.

## 2.2 Corrosion Inhibitor Screening

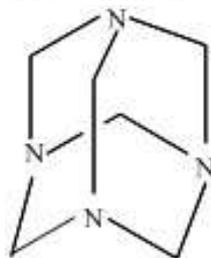
Based on SYT 5273-2000 *Corrosion Inhibitor Performance Measurement for Field Water*, static state coupon weight loss of the above corrosion inhibitors were tested at 80mg/L, 70°C, the result is showed in Table.3.

**Table.3: Corrosion Value of 7 corrosion inhibitors**

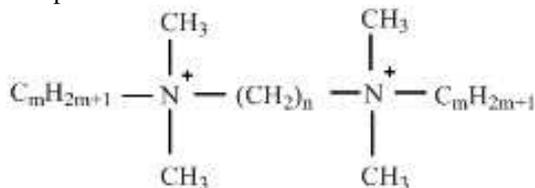
samples	blank	1 <sup>#</sup>	2 <sup>#</sup>	3 <sup>#</sup>	4 <sup>#</sup>	5 <sup>#</sup>	6 <sup>#</sup>	7 <sup>#</sup>
corrosion rate, mm/a	0.0321	0.0113	0.0072	0.0088	0.0044	0.0135	0.0081	0.0068
corrosion resistant percent,%	/	64.8	77.6	72.6	86.3	57.9	74.8	78.8

2#, 4#, 6#,7# have good corrosion inhibitor capability than the other 3 samples, it was considered that the big differences of the molecular structure is the main reason of corrosion inhibitor capability.

1# (Urotropine) is a tetramer, which has the bellowed molecular structure (Fig. 1). There is N atom in urotropine molecule adhering on metal surface, which has the effect of geometric coating. It can reduce the available coverage of corrosion [3]. Single corrosion inhibitor has low corrosion inhibitor percent owing to the bigger cyclic formula, which has steric hindrance effect. So the low coverage of corrosion inhibitor doesn't have obvious corrosion inhibitor effect and it will erode the metal when its' content exceed some specified value. [4]

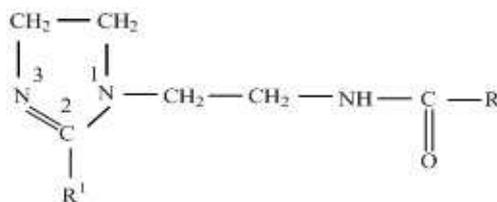
**Fig.1: Urotropine Molecule Structure**

2# (Gemini quaternary ammonium) has the following molecule structure as is shown in Fig.2. It has 2 hydrophilic groups and 2 hydrophobic groups. Such molecule structure can decrease the surface tension of water solution obviously and is compatible with anionic surfactant. Long chain alkyl non-polar group can form a hydrophobic resist film on metal surface, which can prevent the contact of corrosion ion and metal surface.[5]



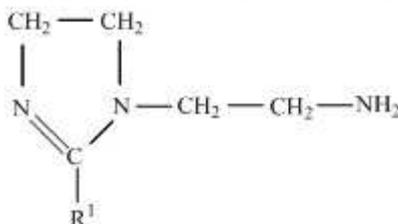
**Fig.2: Gemini Quaternary Ammonium Molecule Structure**

3# (asphalt imidazoline) has the following molecule structure as is shown in Fig.3. There is a sp<sup>2</sup> hybrid orbital in 3-N which doesn't participate in bonding, the lone paired electron is prone to form co-ordination bond with the empty d orbital. Absorption film on the surface of carbon steel can inhibit the metal corrosion affectively.



**Fig.3: Asphalt imidazoline Molecule Structure**

4# (amino-ethyl-imidazoline) has the following molecule structure as is shown in Fig.4. Hydrophobic group R1 can form tight film on metal surface which inhibit the contact of corrosion ion and carbon steel. [7] N atom in polar group can form quaternary ammonium with the other corrosion inhibitors which can inhibit corrosion.



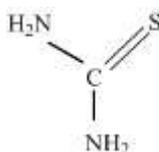
**Fig.4: Amino-Ethyl-Imidazoline Molecule Structure**

5# (formaldehyde) has the following molecule structure as is shown in Fig.5. The O atom in -CHO has two lone paired electrons, which can form co-ordination with Fe d orbital of coupon. The film forming at the coupon can protect the negative pole and reject H<sup>+</sup>, so it can inhibit the corrosion.



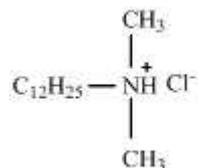
**Fig.5: Formaldehyde Molecule Structure**

6# (thiourea) has the following molecule structure as is shown in Fig.6. The uncommon lone paired electron in N atom can resonance with π electron of C=S, which can increase the electron cloud density and intensify the adsorption of organic cation to metal. The compound of thiourea and imidazoline will have good inhibit effect. Liner chain alkyl group and quinary heterocyclic ring of imidazoline can enter the cylinder channel with the eccentric pattern of thiourea and compound to inclusion compound.[8,9]. The diameter of channel is 0.5nm which can accept and contain the branched and cyclic molecule, such as 6 or more straight chain paraffin, alcohol, ether and aldehyde. Inclusion compound can deposit on the metal surface, and amine group compound to quaternary ammonium which can form one tight film and inhibit the corrosion.



**Fig.6: Thiourea Molecule Structure**

7# (dodecyl-dimethyl-ammonium chloride) has the following molecule structure as is shown in Fig.7. Because there is N<sup>+</sup> in it, so it can form long chain quaternary ammonium. [10] Adverse electric nature ion can absorb on electrode or the interface of solution which changing the nature of electric charge. More and more corrosion inhibitors will be absorbed on electrode surface.[11].



**Fig.7: Dodecyl-Dimethyl-Ammonium Chloride Molecule Structure**

The above 7 corrosion inhibitors can be classified into 4 categories. The first kind is amine inhibitor with N or N<sup>+</sup> in it. It can be converted into quaternary ammonium which absorbing on the surface of metal. When the corrosion inhibitor is added, the Cl<sup>-</sup> or the other anions can absorb on the surface of metal, so the metal surface has negative charge which get the organic cation to absorb on the metal surface. So the H atom is hard to near the metal surface to reduce the metal which can slow down the corrosion. Urotropine, Gemini quaternary ammonium and dodecyl-dimethyl-ammonium chloride can also be attributed to this kind. The second kind is imidazoline corrosion inhibitor with quinary heterocyclic in it. Hydrophilic branched chain R, for example C=O and carbonyl group, hydrophobic branched chain R1 with different carbon chain can form bonding with N in quinary heterocyclic. The hydrophilic branched chain R can improve the water solubility of corrosion inhibitor and also form complex compound with Fe(II) on the metal surface, we call the complex compound resist film. A hydrophobic resist film can be formed far away the metal surface which can not only guard the electrode but also hinder the migration of reagent on corrosive interface. [12] Amino-ethyl-imidazoline and asphalt imidazoline can also be attributed to this kind. The third kind is thiourea corrosion inhibitor. S atom is the polar group center, C=S double bond can supply lone paired electron which form complex compound with empty d orbit of Fe. The resist film absorbing on the metal surface hinders the migration of charge or reagent of corrosion. Thiourea belongs to this kind. The forth kind is aldehyde corrosion inhibitor, O atom is the central atom, C=O double bond can supply lone paired electron which form complex compound with empty d orbit of Fe. The resist film can slow down the metal corrosion. Formaldehyde belongs to this kind.

There are amines in all these four corrosion inhibitors(Gemini quaternary ammonium, amino-ethyl-imidazoline, thiourea, dodecyl-dimethyl-ammonium chloride), quaternary ammonium can be compounded between the amine and the anion which absorbing on the metal surface to control corrosion. At the same time the C=N or C=S double bond can link with empty d orbit of Fe atom to form a resist film on the metal surface. The resist film can not only increase the thickness of absorption layer but also improve the inhibition of corrosion, for example the disperse ability, wettability and permeability.

At 4 elements and 2 levels, a orthogonal array L8(27) was designed to evaluate the 4 corrosion inhibitors, the result is shown below.(Table.4 Table.5)

**Table.4: Element-Level**

Number group	2 <sup>#</sup> , mg/L	4 <sup>#</sup> , mg/L	6 <sup>#</sup> , mg/L	7 <sup>#</sup> , mg/L
1	30	30	30	30
2	50	50	50	50

**Table.5: Orthogonal array L8(27)**

Number group	2 <sup>#</sup> mg/L	4 <sup>#</sup> mg/L	6 <sup>#</sup> mg/L	7 <sup>#</sup> mg/L	Corrosion rate mm/a	Corrosion inhibition rate %
1	1	1	1	1	0.0028	91.3
2	1	1	2	2	0.0103	67.9
3	1	2	1	1	0.0065	79.8
4	1	2	2	2	0.0037	88.5
5	2	1	1	2	0.0098	69.5
6	2	1	2	1	0.0036	88.8
7	2	2	1	2	0.0041	87.2
8	2	2	2	1	0.0115	64.2

We can know from the above result, No.1, 4, 6, 7 groups have better inhibition corrosion ability and the inhibition corrosion percent is up to 87%, among them the No.1 is the highest inhibition corrosion percent 91.3% and the other 3 have poor inhibition corrosion ability. We can also conclude from the result that combination corrosion inhibitor having the same component but the different proportion has distinct corrosion resistant ability. When the proportion

of 2#:4#:6#:7# is 1:1:1:1 (30mg/L), they have synergistic effect to enhance inhibition corrosion effect. 2# (Gemini quaternary ammonium) and 4#( amino-ethyl-imidazoline) have both hydrophilic group and hydrophobic group, it can not only improve the water solubility of imidazoline but also compound with anion to generate quaternary ammonium polymer. The resist film absorbing on the metal surface can forbid the scale deposit of ion on it. 6#(thiourea) can complex with imidazoline to generate inclusion complex or clathrate to inhibit, the molecule reaction formula is shown in Fig.8.

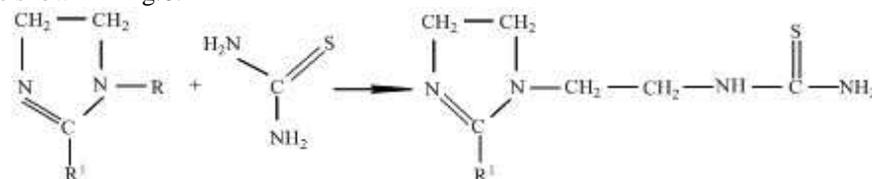


Fig.8: Molecule reaction formula of imidazoline and thiourea

In addition after the combination of imidazoline and thiourea, they will have negative catalytic effect.<sup>[13]</sup> This effect can inhibit the action of anode and cathode, lift the activation energy and enhance the absorption of imidazoline organic cation to metal.

7#(dodecyl-dimethyl-ammonium chloride) can combine with imidazoline to generate long chain quaternary ammonium polymer which has stronger absorption ability on the metal. The reaction molecule formula is shown in Fig.9. Besides the corrosion inhibitor has good water solubility and the hydrophobic group's barrier properties can make it difficult for depolarizer to reach the metal surface, so the corrosion rate slows down. The longer carbon chain and longer hydrophobic group the imidazoline have, the stronger hydrophobicity and shielding effect it will have. [14,15]

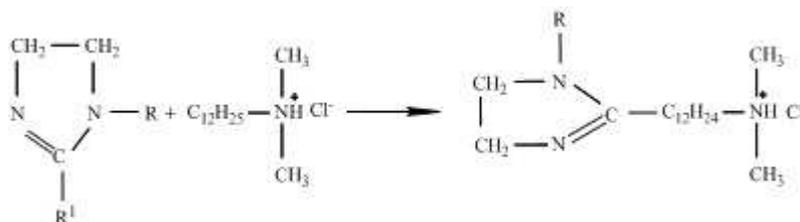


Fig.9: Molecule reaction formula of imidazoline and dodecyl-dimethyl-ammonium chloride to generate quaternary ammonium

So 2#, 4#, 6#, 7# four kinds of corrosion inhibitors will have synergetic effect after combination to stimulate absorption and compensate the limitation of the each one. [16,17] One reason is, the polar group's absorption can change the distribution of charge and boundary character, so the activation energy is lifted and the corrosion speed slows down. The other is, hydrophobic resist film is formed by non-polar group on the metal surface to strengthen corrosion inhibition.

### 2.3 Temperature factor

According to practical measurement, bottom hole temperature is between 110~130°C, the temperature of most serious corrosive point is between 70~110°C. Temperature tolerance test is run at different temperature and same concentration 80mg/L of best corrosion inhibitor using field water sample. The result is showed in Fig.10.

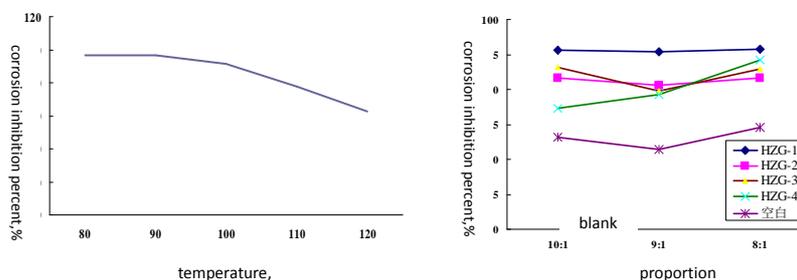


Fig.10: Relation curve of 1# temperature and corrosion inhibition percent

Fig.11: Suitability of different corrosion inhibitors with FC at 120°C

Fig.10 shows us that 1# corrosion inhibitor's corrosion resistant percent decrease with temperature's rising, the most corrosion resistant percent are almost above 90%, but when the temperature rises up to 120 °C, the corrosion resistant percent decreases to 62.9%. So the ordinary corrosion inhibitors have poor temperature tolerance. The reason is that temperature rise accelerates resolution of compounded corrosion inhibitor to improve the corrosion resistant ability,

but the desorption action is intensified with the temperature rise at the same time, so it broaden the contact area of corrosive medium and metal surface to accelerate dissolution and decrease corrosion resistant percent.

So the (FC)[18] was chosen to compound with 1#, 4#, 6#, 7# to improve the temperature tolerance of corrosion inhibitor. At 120°C and the concentration is 80mg/L, optimization test was run at different proportion using field water sample. 1#:FC was labeled HZG-1, 4#:FC was labeled HZG-2 and 6#:FC was labeled HZG-3, 7#:FC was labeled HZG-4. Four kinds of compounded corrosion inhibitors were compared with corrosion inhibitor with no FC in. The corrosion inhibition effect evaluated between them and the result is as follows. (Fig.11) We can know that the temperature tolerance of corrosion inhibitors were enhanced obviously after the addition of FC, and the corrosion resistant percent can reach to 87%. When (1#, 4#, 6#, 7#):FC=8:1, the temperature tolerance of corrosion inhibitors attain the best performance, and the corrosion resistant percent can get up to 90%. So the addition of FC can improve the temperature tolerance of corrosion inhibitors. The reason can be attributed to:

The molecule structure of fluorine-carbon imidazoline is shown in Fig.12. R1 is on behalf of fluoro-group. F atom in fluorine-carbon imidazoline has strong electron affinity and single bond energy, it can bond with empty d orbit of Fe atom and adhere to  $\pi$  bond in quinary heterocyclic ring of imidazoline which can have the tack claw effect. Besides that the strong repulsion force among F atoms forces F branched chain to stretch, and force the F chain which stretch towards solution arrange in eccentric pattern [19]. This can protect all chemical bonds from damage, improve its' temperature tolerance, all these make it have high surface activity, high thermodynamic stability and high chemical stability. Moreover we can also know that the fluorine-carbon imidazoline has the same molecule structure with imidazoline. There is one lone paired electron on 3-N, and this make fluorine-carbon imidazoline have good coordination activity and hydrophobic lipophobic capability. On one hand fluorine-carbon imidazoline can generate coordination complex with transition metal Fe(II) which depositing metal surface[20, 21], on the other hand the non-polar group of corrosion inhibitor absorbed can form a hydrophobic film on metal surface which inhibiting the transfer of charge and substance ( steric effect) and slowing down the corrosion. So the addition of fluorine-carbon imidazoline will strengthen the high temperature tolerance and adsorption performance.

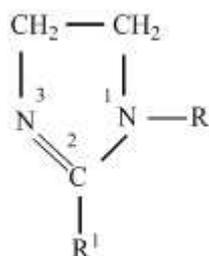


Fig.12: Molecule Structure of fluorine-carbon imidazoline

#### 2.4 Concentration factor and compatibility

To increase the benefit and cost ratio, four formulas were evaluated using field water sample. The result is shown in Fig13 and Fig.14.

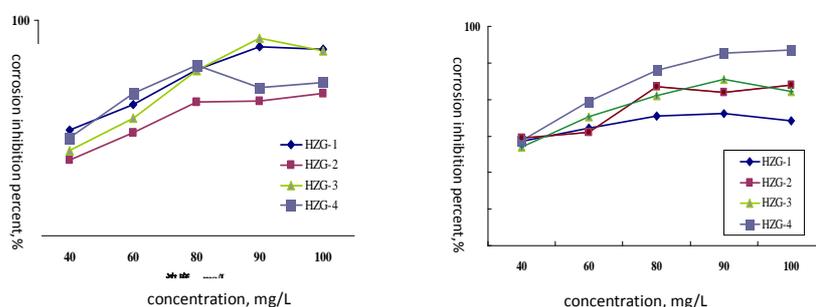


Fig.13: Relation curve of concentration and corrosion inhibition percent on Y60-81X

Fig.14: Relation curve of concentration and corrosion inhibition percent on Y63-69

As is shown in Fig.13 and Fig.14, at 90mg/L, formula HZG-1 using on Y60-81X has high corrosion inhibition percent 92%, but for Y63-69 the corrosion inhibition percent is only 76%; HZG-3 using on Y60-81X has high corrosion inhibition percent 95%, but for Y63-69 the corrosion inhibition percent is only 85%. At 100mg/L, formula HZG-4 using on Y60-81X has low corrosion inhibition percent 80%, but for Y63-69 is 93%.

The result shows that one formula has different effect used on different well. So the formula and concentration should be varied with the applied high temperature oil wells. When the corrosion inhibition effect is steady, the concentration is recommended.

## RESULTS AND DISCUSSION

On the basis of laboratory experiment, a series of HZG corrosion inhibitors were applied on 10 wells site using the periodical injection pattern. (Table.6) The average corrosion inhibition percent is 82%.

**Table.6: Operation effect data list**

Serial number	well No.	Recommended formula	Total iron		Corrosion inhibition percent%
			before	after	
1	Y63-38	HZG -1	17.30	2.41	86.1
2	Y63-43	HZG -2	6.08	1.12	81.6
3	Y63-69	HZG -2	3.90	0.30	92.3
4	Y63-84	HZG -3	21.60	3.54	83.6
5	Y63-100	HZG -4	3.14	0.97	69.1
6	Y60-41	HZG -1	0.96	0.22	77.1
7	Y60-8	HZG -1	0.25	0.00	100.0
8	Y60-81x	HZG -4	1.38	0.48	65.2
9	G59-13	HZG -3	0.45	0.12	73.3
10	Y9-24	HZG -1	17.0	1.20	92.9

## CONCLUSION

(1) Coupon weight loss test shows that Gemini quaternary ammonium, amino-ethyl-imidazoline, thiourea and dodecyl-dimethyl-ammonium chloride each has better corrosion inhibition effect. That's because the corrosion inhibitor can form a resist film on the metal surface.

(2) The series of HZG corrosion inhibitors using fluorine-carbon imidazoline as the essential material has good high temperature tolerance, the limit of temperature can get to 100°C, the average corrosion inhibition percent is 82%.

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