Analysis on the source of scale-forming ions in water injection wells of No.1 structure in Nanpu Oilfield

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Abstract. In order to define the working in the Nanpu oilfield no. 1 injection Wells into scale ion source structure, introducing the Stiff - Davis, prediction of calcium carbonate scale, combining this method with actual production, the scale formation prediction model is set up, find out critical calcium ions concentration, calculated the critical calcium content. According to the content of nanpu oil field in three-phase water outlet ion data, using linear regression method, set up at different times of calcium ion content change curve, compared with critical calcium ion content, find the fouling ion source. Through research shows that working in the nanpu oilfield no. 1 main scale structure type is calcium carbonate scale, the main scale ion Ca^{2+} and HCO_3^- from high pressure well liquid.

Keywords: Stiff-Davis method; Calcium carbonate scale formation; Critical calcium ion concentration; High density pressure well liquid.

1. Introduction
No.1 structure in Nanpu Oilfield is in the stage of water injection development, and serious scaling occurs in the wellbore pipeline and bottom hole of water injection well. Scaling reduces the inner diameter of pipeline and the cross-sectional area of water flow, which leads to the increase of water injection pressure and affects the water injection efficiency. Combined with the actual scaling situation of water injection wells in No.1 structure of Nanpu Oilfield, the scaling trend prediction model suitable for No.1 structure of Nanpu Oilfield was selected, and the Stiff-Davis method was introduced to predict calcium carbonate scaling.

2. Scaling status of water injection wells in No.1 structure of Nanpu Oilfield
From 2012 to April 2013, scaling phenomenon was found in many water injection wells during the operation of No.1 structure in Nanpu Oilfield, and the shaft scaling was serious. A total of 10 scaling water injection wells were found, including 2 in Nanpu Oil Production Zone 1, 1 in Nanpu Oil Production Zone 2 and 7 in Oil Production Zone 3. There are 109 water injection wells in Nanpu Oilfield, including 72 water injection wells in No.1 structure, accounting for 66% of the water injection wells. The water source of water injection wells in No.1 structure comes from the sewage treatment station in No.1 oil production area of Nanpu Oilfield.

See fig. 1 for statistics of scaling of water injection wells in No.1 structure of Nanpu oilfield.
Figure 1. Scale statistics of injection wells in No.1 structure of Nanpu Oilfield

See fig. 2 for the flow direction of water injection source in injection well of No.1 structure in Nanpu oilfield

Figure 2. Trend map of water injection source of injection well of No.1 structure in Nanpu Oilfield

3. Type of scale
Spectral analysis of scale samples from Nanpu injection wells is shown in Figure 2.
It can be seen from the figure that the scale type is mainly calcium carbonate and a small amount of magnesium carbonate. Magnesium carbonate is more soluble than calcium carbonate, and its solubility in distilled water is four times greater than that of calcium carbonate. Therefore, for most water containing both magnesium carbonate and calcium carbonate, any condition that reduces the solubility of magnesium carbonate and calcium carbonate will first form calcium carbonate scale.

The water quality of every link of Nanpu No.1 structure water injection source was analyzed, and the report showed that calcium ion was generally 3-8 times of magnesium ion. Therefore, the main scale type of water injection wells in Nanpu No.1 structure is calcium carbonate scale.

4. Prediction model
The scale samples taken from scaling wells in Nanpu Oilfield were dried, burned and dissolved in acid, and the scale samples were tested by acid titration. The test results showed that the scale types were mainly calcium carbonate, a small amount of magnesium carbonate, a small amount of sulfate scale, iron compound scale and organic scale, and the main scale-forming ions were Ca$^{2+}$ and HCO$_3^-$ [1].
4.1. **Prediction of calcium carbonate scaling by Stiff-Davis method [2]**

Scale formation of calcium carbonate is predicted according to Stiff-Davis method (see Formula 1)

\[ \text{SI} = A - \text{pCa} - \text{pAlk} - K \]  

(1)

In the formula:
- \( A \) —— Actual measured PH value of water sample;
- \( \text{pCa} \) —— The negative logarithm of \( \text{Ca}^{2+} \) concentration in mol/L;
- \( \text{pAlk} \) —— The negative logarithm of total alkalinity, which is the sum of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) concentrations in water, and the concentration unit is mol/L;
- \( K \) —— Stiff-Davis constant is a function of temperature and ionic strength;
- \( \text{SI} \) —— Saturation index, also called scaling index.

When \( \text{SI} \) is less than 0, CaCO₃ is unsaturated and will not scale. When \( \text{SI} \) is greater than 0, CaCO₃ is saturated and may scale.

First, the formula (2) is obtained by transforming the formula (1)

\[ \text{pCa} = A - \text{pAlk} - K - \text{SI} \]  

(2)

When \( \text{SI} = 0 \), that is, when calcium carbonate is saturated in water, the formula (3) for calculating the critical calcium ion concentration can be derived

\[ \text{C}_{\text{cr}} = 10^{-\text{pCa}} = 10^{-(A - \text{pAlk} - K - \text{SI})} \]  

(3)

Then, the formula (4) for calculating the critical calcium ion content can be obtained

\[ \text{N}_{\text{cr}} = \text{C}_{\text{cr}} \times 40 \text{g} \]  

(4)

If the critical value of calcium ion content at different temperatures can be calculated and compared with the calcium ion content in water-based analysis, it can be predicted whether there is scaling tendency of calcium carbonate in No.1 structure of Nanpu Oilfield.

4.2. **Definite solution condition**

It can be seen from formula 1-1 that the factors affecting calcium carbonate saturation index mainly depend on \( \text{pCa} \), \( \text{pAlk} \), \( a \) and \( K \).

\( K \) is a constant, which can be obtained by looking up the table. It is necessary to know the ionic strength, which \( I \approx \text{TDS} \text{ (mg/L)} / 58400 \). TDS is the total salinity [2].

The water source of injection well in Nanpu No.1 structure, that is, the water delivered outside the sewage treatment station of No.1 oil production area in Nanpu Oilfield, has been kept at PH 7.0, so \( A = 7.0 \).

Under normal pressure, the total salinity and alkalinity of sewage from No.1 structure in Nanpu Oilfield from April 2010 to February 2013 are taken as the research objects (see Figure 5 and Figure 6)
Figure 5. Change curve of total alkalinity

It can be seen from the above figure that the total salinity and total alkalinity of sewage from No.1 structure in Nanpu Oilfield change smoothly, and it can be obtained by calculation that the average total salinity is 3,701 mg/L; Average total alkalinity = 19.58 mmol/l.

By verifying the maximum and minimum values of total salinity and total alkalinity, it is found that the total salinity and total alkalinity have little effect on calcium carbonate scaling in the actual production process and can be ignored, so the total salinity and total alkalinity can be averaged.

5. Model solving
When TDS=3701mg/L, I≈0.06 is calculated, and K values at different temperatures are found (see Table 1)

Table 1. K value at different temperatures

| Temperature (°C) | 10 | 20 | 25 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
|-----------------|----|----|----|----|----|----|----|----|----|----|
| K               | 2.6| 2.4| 2.2| 2.1| 1.9| 1.7| 1.6| 1.3| 1.2| 1.0|

When total alkalinity =19.58mmol/L, the negative logarithm of total alkalinity Palk=1.71 can be obtained by calculation.

According to the formulas (1-3, 1-4), the critical calcium ion concentration and content at different temperatures can be calculated (see Table 2)

Table 2. Critical calcium ion content at different temperatures

| Temperature (°C) | P裢常数 | K | Pal | KPal | Pca | Critical calcium ion concentration | Critical calcium ion content |
|-----------------|---------|----|-----|------|-----|-----------------------------------|----------------------------|
| 10              |         | 2.6| 2.69| 2.04 | 81.6|
| 20              |         | 2.4| 2.89| 1.29 | 51.6|
| 25              |         | 2.2| 3.09| 0.81 | 32.4|
| 30              |         | 2.1| 3.19| 0.64 | 25.6|
| 40              |         | 1.9| 3.39| 0.41 | 16.4|
| 50              |         | 1.7| 3.59| 0.26 | 10.4|
| 60              |         | 1.6| 3.69| 0.2  | 8   |
| 70              |         | 1.3| 3.99| 0.1  | 4   |
| 80              |         | 1.2| 4.09| 0.08 | 3.2 |
| 90              |         | 1  | 4.29| 0.05 | 2   |

Because the conditions of water-based analysis are normal pressure and room temperature, and the room temperature is close to 20°C. At 20°C and normal pressure, the critical scaling calcium ion content of No.1 structural sewage in Nanpu Oilfield is 51.6 mg/L.
6. Source analysis of calcium ion
According to the flow direction of water injection source of No.1 structural injection well in Nanpu Oilfield, the source of scaling ions was traced back upstream from the water delivery outside the No.1 oil production area in Nanpu Oilfield by using the method of reverse push.

6.1. Water-based analysis of water outlet of three-phase separator
Because the water from the water outlet of the three-phase separator passes through the crude oil dehydration and sewage treatment system during the water transfer from Nanpu 1-1 artificial island, the only foreign liquids entering the system in this process are Laoye temple sewage and added chemicals, the main chemicals are: Three-phase demulsifier is polyether, reverse demulsifier is polyquaternary ammonium salt, coagulant and coagulant aid are inorganic polyaluminium chloride and bactericide is biquaternary ammonium salt, which do not contain scale-forming ions and basically do not change water property [3].

Moreover, the calcium ion content of Laoye temple sewage is lower than the critical ion content, and the total alkalinity and salinity are close to the average value of external water delivery, so there is no scaling trend under normal pressure (see Table 3).

| Name               | Mg$^{2+}$ mg/L | Ca$^{2+}$ mg/L | HCO$_3^-$ mg/L | CO$_3^{2-}$ mg/L | Total salinity mg/L | Total alkali mmol/L | PH value |
|--------------------|----------------|----------------|-----------------|-----------------|--------------------|--------------------|----------|
| Laoye temple sewage| 12             | 47             | 1235            | 77              | 3146               | 22.80              | 7.0      |

Therefore, the data of calcium ion content in the water outlet of the three-phase separator in the first oil production area of Nanpu Oilfield is analyzed and studied. The change of calcium ion content in a period of time was taken as the research object, and compared with the critical scaling calcium ion content at 20°C and normal pressure.

From July, 2012 to December, 2012, the change of calcium ion content in water outlet of Nanpu 1-1 artificial island in No.1 structure of Nanpu Oilfield is shown in Figures 7, 8 and 9.

**Figure 6.** Change curve of calcium ion content in 1# three-phase separator

**Figure 7.** Change curve of calcium ion content in 2# three-phase separator
Through comparative analysis, it can be seen that the water outlets of the three-phase separators have scaling trends in different degrees, among which the scaling trend of the water outlet of No.2 three-phase separator is serious, that is, the fluid from the third oil production area of Nanpu Oilfield.

6.2. Water-based analysis of system incoming liquid
The comparative analysis of the water outlet of the three-phase separator shows that the system fluid from each oil production area in Nanpu Oilfield has scaling tendency to varying degrees. Therefore, the water property of the system fluid from each production area of Nanpu Oilfield is analyzed. The system fluid from each oil production area of Nanpu Oilfield includes three parts: produced water from oil well, produced water from water source well and kill fluid.

6.2.1. Comparative analysis of produced water from oil wells. Select representative wells in different blocks and horizons as research objects, conduct water-based analysis, and compare and analyze calcium ion content with critical scaling calcium ion content. See tables 4, 5, 6, 7 and 8

| Oil well number | Sampling date | Production horizon | Mg$^{2+}$ mg/L | Ca$^{2+}$ mg/L | HCO$_3^-$ mg/L | CO$_3^{2-}$ mg/L | Total salinity mg/L | Total alkali mmol/L | PH value | Remarks |
|-----------------|---------------|-------------------|----------------|----------------|----------------|----------------|-------------------|-------------------|----------|---------|
| NP11-X130       | 2012.06.09    | NmII              | 6              | 10             | 580            | 85             | 1352              | 12.32             | 7        |         |
| NP1-4A2-P3      | 2012.12.23    | NgII              | 0              | 5              | 968            | 66             | 1810              | 18.04             | 7        |         |
| NP1-4A15-P251   | 2012.06.09    | NgIV              | 2              | 8              | 451            | 42             | 2161              | 8.8               | 7        |         |
| NP1-32C1        | 2013.03.08    | EdI               | 6              | 15             | 1935           | 66             | 4735              | 33.9              | 7        |         |
| NP11-L8-X204    | 2013.03.08    | EdI               | 13             | 7              | 3971           | 131            | 6698              | 69.44             | 8        |         |
| NP11-C1-X206    | 2013.03.08    | EdI               | 17             | 25             | 2069           | 66             | 4530              | 36.09             | 7        |         |
| NP11-X118       | 2012.04.03    | NgII              | 3              | 15             | 601            | 82             | 1367              | 12.58             | 7        |         |
| NP1-4A4-X501    | 2012.05.19    | NgIV              | 1              | 3              | 1133           | 135            | 3339              | 23.06             | 7.5      |         |
| NP118-1         | 2012.08.17    | NgIV              | 1              | 20             | 578            | 62             | 2406              | 11.53             | 7        |         |

| Oil well number | Sampling date | Production horizon | Mg$^{2+}$ mg/L | Ca$^{2+}$ mg/L | HCO$_3^-$ mg/L | CO$_3^{2-}$ mg/L | Total salinity mg/L | Total alkali mmol/L | PH value | Remarks |
|-----------------|---------------|-------------------|----------------|----------------|----------------|----------------|-------------------|-------------------|----------|---------|
| NP12-X812       | 2013.02.24    | EdIII             | 9              | 20             | 400            | 66             | 986               | 8.75              | 7        |         |
| NP12-X805       | 2012.05.14    | EdIII             | 4              | 20             | 2008           | 0              | 5469              | 32.91             | 7.5      |         |
| NP1-29X90       | 2013.02.23    | NgIV              | 33             | 15             | 2402           | 131            | 6450              | 43.74             | 8        |         |
| NP1-29          | 2012.05.24    | NgIV              | 15             | 35             | 1785           | 135            | 6433              | 33.75             | 7        |         |
### Table 6. Analysis of produced water from oil wells in the third oil production area

| Oil well number | Sampling date | Production horizon | Mg2+ mg/L | Ca2+ mg/L | HCO3- mg/L | CO32- mg/L | Total salinity mg/L | Total alkali mmol/L | PH value | Remarks |
|-----------------|---------------|-------------------|-----------|-----------|-------------|-------------|--------------------|---------------------|----------|---------|
| NP13-1942       | 2013.03.03    | EdI               | 6         | 30        | 898         | 0           | 3172               | 14.72               | 7        |         |
| NP13-X1106      | 2012.02.25    | EdI               | 4         | 27        | 3370        | 98          | 9690               | 58.51               | 7        |         |
| NP13-X1058      | 2012.06.17    | NgI               | 1         | 9         | 686         | 34          | 1364               | 12.38               | 7        |         |
| NP13-X1026      | 2012.12.31    | EdII              | 6         | 32        | 3017        | 46          | 6278               | 50.98               | 7        |         |
| NP13-1152       | 2012.10.30    | EdIII             | 2         | 12        | 4088        | 0           | 7626               | 66.99               | 7        |         |
| NP13-X1702      | 2012.12.27    | O                 | 18036     | 32335     | 3863        | 0           | 146759             | 4.5                 |          |         |

Well killing fluid with specific gravity of 1.25 was used for oil test on October 25, 2012. Blowout prevention on December 6th and completion on December 17th.

### Table 7. Analysis of produced water from oil wells in the fourth oil production area

| Oil well number | Sampling date | Production horizon | Mg2+ mg/L | Ca2+ mg/L | HCO3- mg/L | CO32- mg/L | Total salinity mg/L | Total alkali mmol/L | PH value | Remarks |
|-----------------|---------------|-------------------|-----------|-----------|-------------|-------------|--------------------|---------------------|----------|---------|
| NP41-X4536      | 2012.06.08    | EsI               | 3         | 10        | 4599        | 120         | 7114               | 79.38               | 7.5      |         |
| NP42-X4322      | 2013.01.20    | NgI               | 2         | 5         | 740         | 0           | 1595               | 12.13               | 7        |         |
| NP41-4218       | 2013.01.20    | NgII              | 2         | 21        | 723         | 0           | 2168               | 11.84               | 7        |         |
| NP41-4128       | 2012.09.06    | NgIII             | 3         | 11        | 642         | 75          | 1905               | 13.02               | 7        |         |
| NP41-4110       | 2012.09.06    | NmIII             | 7         | 32        | 795         | 105         | 1841               | 16.53               | 7        |         |

### Table 8. Analysis of produced water from oil wells in the fifth oil production area

| Oil well number | Sampling date | Production horizon | Mg2+ mg/L | Ca2+ mg/L | HCO3- mg/L | CO32- mg/L | Total salinity mg/L | Total alkali mmol/L | PH value | Remarks |
|-----------------|---------------|-------------------|-----------|-----------|-------------|-------------|--------------------|---------------------|----------|---------|
| NP23-P2003      | 2012.11.06    | O                 | 163       | 486       | 1062        | 0           | 16399              | 17.41               | 6        | 2012.10.21 Overhaul and completion. Use 1.25 kill hydraulic well. |
| NP23-P2009      | 2011.12.17    | O                 | 272       | 1941      | 125         | 0           | 11847              | 2.05                | 5.5      | On November 24, 2011, the oil was tested, overflowing and replacing 150 cubic meters of 1.25 kill fluid. |
| NP23-P2006      | 2013.01.30    | O                 | 3         | 19        | 2065        | 0           | 5500               | 33.84               | 7        |         |
| NP23-X2110      | 2011.02.07    | NgII              | 1         | 6         | 717         | 0           | 1062               | 11.76               | 7        |         |
| NP23-X2408      | 2013.03.07    | NgII              | 1         | 5         | 485         | 0           | 795                | 7.95                | 7        |         |
| NP23-X2402      | 2012.03.12    | NgIII             | 3         | 47        | 1589        | 0           | 3936               | 26.04               | 7        |         |
| NP23-X2407      | 2011.05.06    | EdI               | 5         | 9         | 2866        | 68          | 4294               | 49.22               | 8        |         |
| NP23-X2411      | 2011.11.30    | EdI               | 4         | 8         | 1610        | 62          | 2486               | 28.44               | 7        |         |
| NP23-X2212      | 2012.08.30    | EdI               | 2         | 22        | 1039        | 286         | 3558               | 26.54               | 8        |         |
According to the above analysis, there is no scaling trend in the produced water of oil wells except the three wells in Ordovician in the third and fifth oil production areas. The three wells are analyzed and studied: First, they all use high density kill fluid; Second, before using high-density kill fluid, the average calcium ion content in historical water analysis is about 20mg/L and not more than 51.6mg/L.

6.2.2. Comparative analysis of produced water from water source wells. The water property of the produced water entering the water source well of the sewage treatment system in Nanpu No.1 Oil Production Zone is analyzed, as shown in Table 9.

Table 9. Analysis of produced water from water source wells in Nanpu Oilfield

| Oil well number | Sampling date | Mg$^{2+}$ mg/L | Ca$^{2+}$ mg/L | HCO$_3^-$ mg/L | CO$_3^{2-}$ mg/L | Total salinity mg/L | Total alkali mmol/L | PH value |
|-----------------|---------------|----------------|----------------|----------------|-----------------|-------------------|-------------------|---------|
| B3              | 2009.12.02    | 3              | 10             | 313            | 0               | 912               | 5.13              | 7       |
| NP23-X2403      | 2009.12.03    | 2              | 6              | 595            | 0               | 976               | 9.75              | 7       |
| NP23-X2540      | 2009.12.03    | 0              | 2              | 563            | 31              | 961               | 10.26             | 7       |
| B1-1            | 2009.12.24    | 2              | 10             | 282            | 31              | 816               | 5.64              | 7       |
| NP23-X2540      | 2010.05.06    | 0              | 2              | 599            | 0               | 908               | 9.82              | 7       |
| NP23-X2403      | 2010.05.06    | 0              | 3              | 570            | 0               | 960               | 9.35              | 7       |
| B7-11           | 2010.05.14    | 1              | 12             | 354            | 16              | 1049              | 6.34              | 7       |
| NP11-X130       | 2010.06.09    | 6              | 10             | 580            | 85              | 1352              | 12.32             | 7       |
| NP23-X2228      | 2012.01.11    | 0              | 4              | 631            | 0               | 955               | 10.35             | 7       |
| NP23-X2245      | 2012.01.11    | 0              | 3              | 581            | 0               | 880               | 9.53              | 7       |
| NP101X8         | 2012.10.23    | 1              | 3              | 547            | 32              | 1189              | 10.02             | 7       |
| NP23-X2228      | 2013.03.07    | 0              | 4              | 293            | 17              | 526               | 5.36              | 7       |
| NP23-X2403      | 2013.03.07    | 0              | 2              | 313            | 0               | 734               | 5.13              | 7       |

The ratio analysis shows that the calcium ion content is lower than the critical scaling calcium ion content, and there is no scaling trend.

6.2.3. Comparative analysis of killing fluid water property. The well killing fluid entering the sewage treatment system of Nanpu No.1 Oil Production Area is analyzed.

6.2.3.1 Component analysis of kill fluid

1) Low density formula (density 1.01-1.20g/cm$^3$): 1% clay anti-swelling agent TRFP-1+1% potassium chloride +0.02% sodium sulfite+water + (0-26%) sodium chloride.

2) High density formula (1.25 ~ 1.35 g/cm$^3$): 1% clay anti-swelling agent TRFP-1+1% potassium chloride +0.02% sodium sulfite+0.2%EDTANa$_2$ (EDTA complexing agent) +0.1% HEC (HEC tackifier) + water + (26-40%) calcium chloride.

It can be seen that the low density kill fluid does not contain calcium ions, while the high density kill fluid contains a large amount of calcium ions.

6.2.3.2 Water-based analysis of kill fluid

Table 10. For water-based analysis of high-density kill fluid.

| Name              | Mg$^{2+}$ mg/L | Ca$^{2+}$ mg/L | SO$_4^{2-}$ mg/L | HCO$_3^-$ mg/L | CO$_3^{2-}$ mg/L | Total salinity mg/L | Total alkali mmol/L | PH value |
|-------------------|----------------|----------------|------------------|----------------|-----------------|--------------------|---------------------|----------|
| High density kill fluid | 2907           | 182156        | 34445            | 116124        | 0               | 757864             | 1903.04             | 6.50     |

It can be seen from the above table that scaling ions of injection wells in No.1 structure of Nanpu Oilfield originate from calcium chloride in high-density kill fluid.
7. Summary
(1) In No.1 structure of Nanpu Oilfield operation area, the main scale type is carbonate scale, most of which is calcium carbonate scale, and there is a small amount of magnesium carbonate scale, which mainly forms scale ions Ca²⁺ and HCO₃⁻.

(2) By using Stiff and Davis methods, the critical scaling calcium ion content of water conveyance outside No.1 structure in Nanpu Oilfield operation area at normal pressure and room temperature is calculated to be 51.6mg/L, which can be compared with the calcium ion content in the water-based analysis report to judge whether there is scaling trend.

(3) It is determined that the main scaling ions Ca²⁺ and HCO₃⁻ in water injection wells of No.1 structure in Nanpu Oilfield come from high-density kill fluid, which has defined the goal and laid a foundation for scaling control of No.1 structure water injection wells in Nanpu Oilfield.

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