# The chemical reasons why some wells in Lübeck (Germany) are blocked

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# Abstract

This report aimed at analyzing the chemical reason for blockage of some wells in Lübeck, Germany. For this purpose, a total of 10 different types of wells were examined and the physical and chemical property of ground water in these 10 wells were measured through a wide range of experiment. After that, the experiment data was analyzed by three software (Aqion, PhreeqC and Diagramme) to find out which types of wells are prone to chemical precipitation, leading to blockage. Moreover, this report also aimed to find out some relationships between different parameters.

# 1 Introduction

## 1.1 Water and wells in Lübeck, Germany

The quality of water in Lübeck is recorded by a website, called "Stadtwerk, Lübeck ". Some important index, including anion and cation concentrations, are recorded on the website and can be checked for research.

In recent years, some wells were blocked, most of which were due to chemical and physical reasons; thus, the local government wanted to know precisely why this blockage happened and have planned to change some wells. In this paper, however, only *Chemical reasons* were taken into consideration.

## 1.2 Research purposes

In this research, many sample wells will be tested via several simple experiments to examine the thermodynamic stability of ground water in each well and find out which kinds of wells are more likely to be blocked by sediment.

Moreover, the correlations between different index should also be recognized. If the main causes of blockage can be found, it is easier to control some chemical concentration of water and is easier to choose the types and sites of wells.

# 2 Raw data

In this paper, a total of 10 types of wells in Lübeck were examined as quickly as possible to guarantee precision. This includes the temperature, conductivity, the concentration of oxygen, PH-value and some main ions, such as $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $SO^{2-}$ and $Cl^-$. In addition, some other parameters like the balance of base, which is determined by the acid capacity (4.3) and the base capacity (8.2), can be calculated by the concentrations of $HCO_3^-$ and free $CO_2$.

Table 2.1, 2.2, 2.3 show the entire data of ground water:

Table 2.1 The temperature, PH, conductivity, EH-value and $O_2$ of the ground water

| Name | T°C | pH | c25°C[μS/cm] | eH(mv) | $O^2$(mg/L) |
|------|-----|-----|--------------|--------|-----------|
| Brunnen 3.1 | 9.5 | 7.31 | 800 | -140 | 0.1 |
| Brunnen 4.3 | 9.6 | 7.35 | 607 | -175 | 0.1 |
| Brunnen 5 | 9.5 | 7.27 | 639 | -79 | 0.2 |
| Brunnen 6 | 9.2 | 7.36 | 700 | -154 | 0.1 |
| Brunnen 7 | 9.6 | 7.51 | 500 | -96 | 0.2 |
| Brunnen 8 | 9.7 | 7.36 | 700 | -164 | 0.1 |
| Brunnen 9 | 9.8 | 7.56 | 600 | -143 | 0.1 |
| Brunnen 10 | 9.3 | 7.34 | 672 | -161 | 0.1 |
| Brunnen 11 | 9.6 | 7.32 | 649 | -168 | 0.2 |
| Brunnen 12 | 10.3 | 7.48 | 779 | -185 | |

As can be seen in the table, these values are very close to each other in different wells, despite some conductivity and the eH-value. The oxygen concentration was also very low, meaning that **the ground water was not fresh and was reducing**.

Table 2.2 Some ions in the ground water

| Name | Ca$^{2+}$ | Mg$^{2+}$ | Na$^{+}$ | K$^{+}$ | HCO3$^{-}$ | CO$_2$ | Cl$^{-}$ | Br$^{-}$ | SO4$^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|
| Brunnen 3.1 | 128 | 16.9 | 18.6 | 2.7 | 425 | 28.2 | 27.9 | 0.07 | 46.4 |
| Brunnen 4.3 | 122 | 9.7 | 13.4 | 2.6 | 365 | 17.6 | 29.5 | | 51.4 |
| Brunnen 5 | 117 | 8.8 | 9.3 | 1.9 | 336 | 14.5 | 26.5 | | 46.4 |
| Brunnen 6 | 119 | 9.4 | 12.4 | 3.5 | 318 | 19.4 | 32.7 | 0.05 | 64.7 |
| Brunnen 7 | 91.8 | 6.7 | 7.2 | 1.6 | 289 | 12.8 | 12 | | 18.6 |
| Brunnen 8 | 103 | 11.3 | 17.5 | 2.3 | 350 | 20.7 | 30.7 | 0.05 | 22.5 |
| Brunnen 9 | 88 | 4.7 | 9.8 | 1.5 | 232 | 7.48 | 20.6 | | 44.9 |
| Brunnen 10 | 120 | 8.8 | 10.2 | 1.9 | 356 | 15.8 | 27.2 | | 50.2 |
| Brunnen 11 | 117 | 11.3 | 12 | 2.1 | 406 | 17.2 | 15.2 | | 24.1 |
| Brunnen 12 | 120 | 20.3 | 18.2 | 3.7 | | 15.4 | 13.7 | | 16.4 |

*All the unit is in mg/L

As shown in the table, cations vary considerably in each sample water.

Table 2.3 Redox potential of the groundwater

| Name | pH | eH | O$_2$ | DOC | Fe | NH$_4$ | NO$_2$$^{-}$ | NO$_3$$^{-}$ |
|---|---|---|---|---|---|---|---|---|
| Brunnen 3.1 | 7.31 | -140 | 0.1 | 2.9 | 3.09 | 0.37 | | |
| Brunnen 4.3 | 7.35 | -175 | 0.1 | 1.8 | 1.71 | 0.16 | | |
| Brunnen 5 | 7.27 | -79 | 0.2 | 2.3 | 1.53 | 0.38 | | |
| Brunnen 6 | 7.36 | -154 | 0.1 | 1.7 | 2.08 | 0.2 | | |
| Brunnen 7 | 7.51 | -96 | 0.2 | 1.8 | 1.34 | 0.15 | 0.01 | 0.4 |
| Brunnen 8 | 7.36 | -164 | 0.1 | 1.7 | 2.32 | 0.24 | | |
| Brunnen 9 | 7.56 | -143 | 0.1 | 1.6 | 1.04 | 0.15 | | |
| Brunnen 10 | 7.34 | -161 | 0.1 | 2.0 | 1.53 | 0.34 | 0.01 | |
| Brunnen 11 | 7.32 | -168 | 0.2 | 1.8 | 2.18 | 0.2 | 0.01 | |
| Brunnen 12 | 7.48 | -185 | | 2.5 | 3.22 | 0.69 | 0.02 | |

*the unit of anion concentrations is in mg/L,

The Redox potential also vary slightly in each sample, especially in the well 5 and the well 7 and the eH-value were extremely higher in this two wells.

# 3 Methods for analysis

## 3.1 Software

In the analysis, a total of three software was used, namely Aqion, PhreeqC and Diagramme. Each software is based on thousands of thermodynamic equations or a huge databank, which is very useful to calculate different trace elements (other than raw data, for example the amount of Calcite can be calculated although this value is not provided in raw data) and the correlations between different index. With the help of these 3 software, whether sediment exists and how much it will be can also be determined in detail.

## 3.2 Chemical principles

In the whole experiment and analysis, the most important index was SI (saturation index, determining the sediment rate and the total sediment amount) which should be calculated several times. In order to achieve this purpose, ion strength should be calculated at first.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i \, z_i^{\,2}$$

ci is the concentration of each anion / cation;
$z_i$ is the valence of each anion/ cation.

Ion strength reflects how charges a solution is and has a great impact on the ion activity. Usually, the ion activity is just a function of ion strength of a solution and its valence. Although there are a large number of functions for ion activity exiting nowadays, in this analysis, only the model from Guggenheim und Davies was mainly used.

$$\lg(f) = 0.5 * z_i^{\,2} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} \right) - 0.3 * I$$

I is the ion strength, usually in mg/L;

$z_i$ is the valence of each anion/ cation.

These 2 functions, in most cases, will be used several times, until all the ion activity correspond to the real situation with error less than 5%. Sometimes, the acceptable error is even less than 2%. Fortunately, all the sophisticated calculation can be accomplished by the software.

Then the saturation index can be determined in the following simple equation:

$$SI = \log\left(\frac{I_{AP}}{K}\right)$$

where K is the balance constant;

$I_{AP}$ is ion productivity (multiplication of all ion activitis)

If SI > 0 the certain chemicals will precipitate; by contrast, if SI < 0, the chemicals will not precipitate.

# 4 Result

## 4.1 The results from Diagramme

Firstly, Diagramme (Simler 2019) was used to analyze the data. In the first step, all the raw data was input into the software to examine and guarantee that the error was less than 2%. Based on the raw data, two pictures were then made for analysis. The first one was a diagram (4.1.1) made by professor Dr. Külls (2019) about relationship of main cations (Mg, Ca and Na+K) while the second one was a diagram (4.1.2) regarding main anions (CO3+HCO3, SO4 and Cl+NO3). [1]
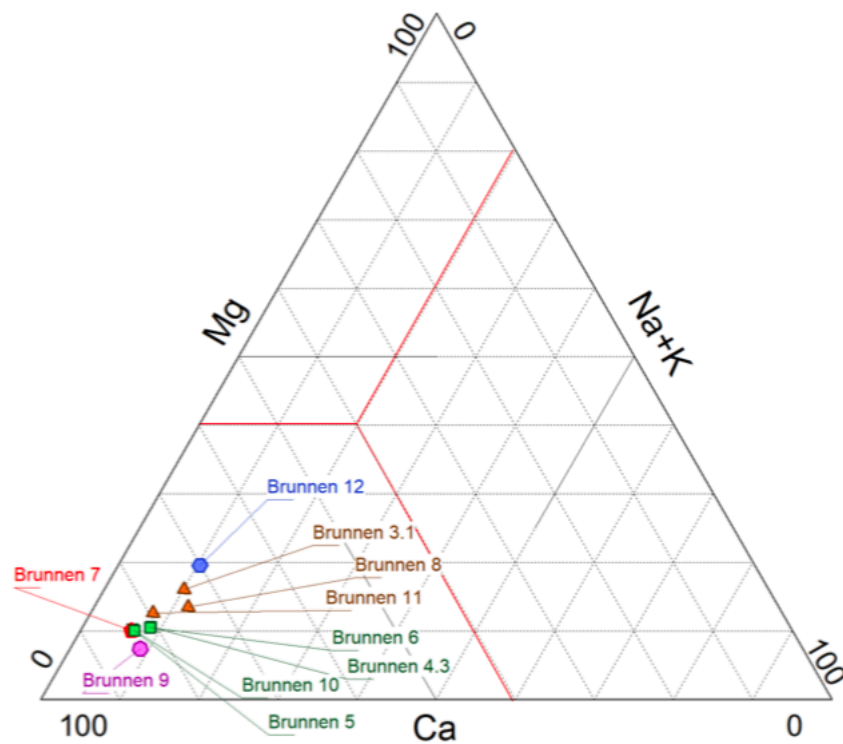


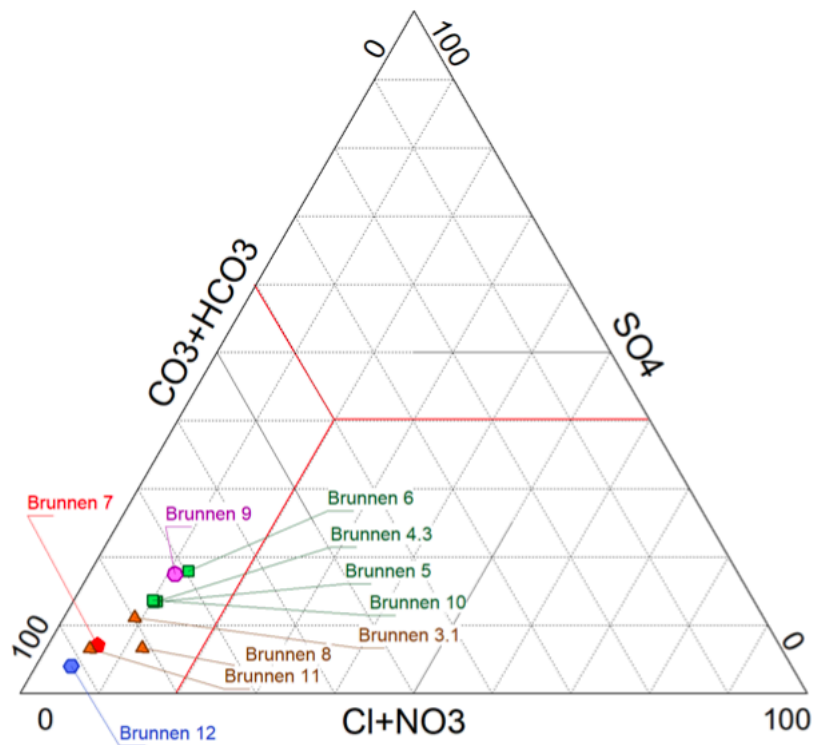Diagram 4.1.1 The proportions of Cation in the water [1]

Diagram 4.1.2 The proportions of anion in the water [1]

Overall, the proportions of cation and anion in each sample did not vary greatly (all in the bottom-left corners). However, it is remarkable that the ground water (GW) in well 9 had the largest proportion of Calcium （about 85%） and second largest percentage of Sulfate. By comparison, the proportion of Calcium in the ground water from well 12 was lowest, at about 70%, but the percentage of hydrogen carbonate/carbonate (CO3+HCO3) from the ground water in this well was highest amongst the 10 wells, reaching more than 90%. **This two well are two extremes, representing two main types of well.**

In diagram 4.1.1, the percentages of cations in the GW from well 4.3, 5, 6, 7, 10 were nearly the same (about 80% Calcium, and 10% Mg and 10% Na + K), while those of cations in well 3.1, 8, 11 were different with the proportions of calcium being slightly lower.

Similarly, in diagram 4.1.2, the GW in well 6, 4,3, 5 ,10 had similar proportions of anions with the percentage of SO4 being around 15% and hydrogen carbonate

being around 75% while the figure for GW in well 3.1, 6, 11 had higher proportion of hydrogen carbonate but lower percentage of sulfate. The percentage of Na + K was nearly the same in GW from those 10 wells, at about 10%.

It should be mentioned that the percentage of cations in the GW of well 7 resembled that of GW in well 9; however, its proportion of anions was similar to another group.

Therefore, these 10 types of well can now be classified into 2 big groups and well 7 was an exception.

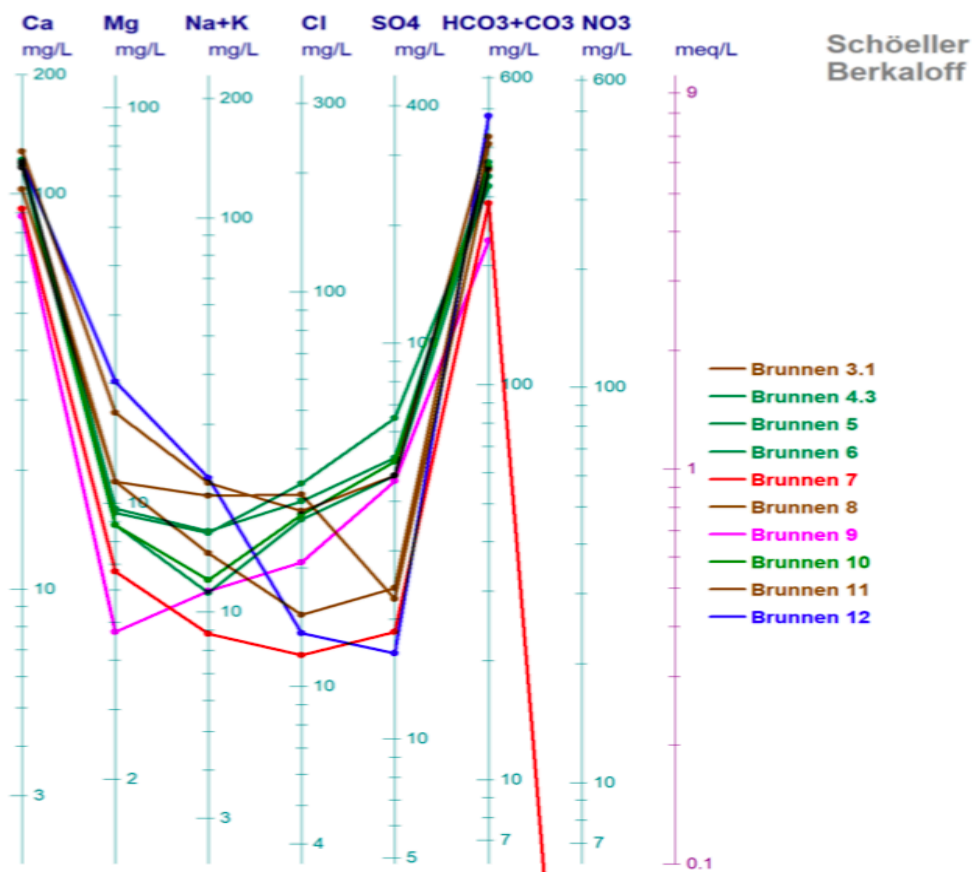This information can also be expressed by **Schoeller Diagramm**[1], but the units are mg/L.



Diagram 4.1.3 Cations and anions analysis by Schoeller Diagramm [1]

In this diagram, it is clearer that the amount of Calcium was nearly same in wells but that of Mg, Na+K, Cl, SO4 HCO3+CO3 varied greatly. This was very important

for our analysis. More importantly, it was also clear that, although the first two groups did exist, **the line of well 7 is quite different to other 9 lines, leading to a third group.**

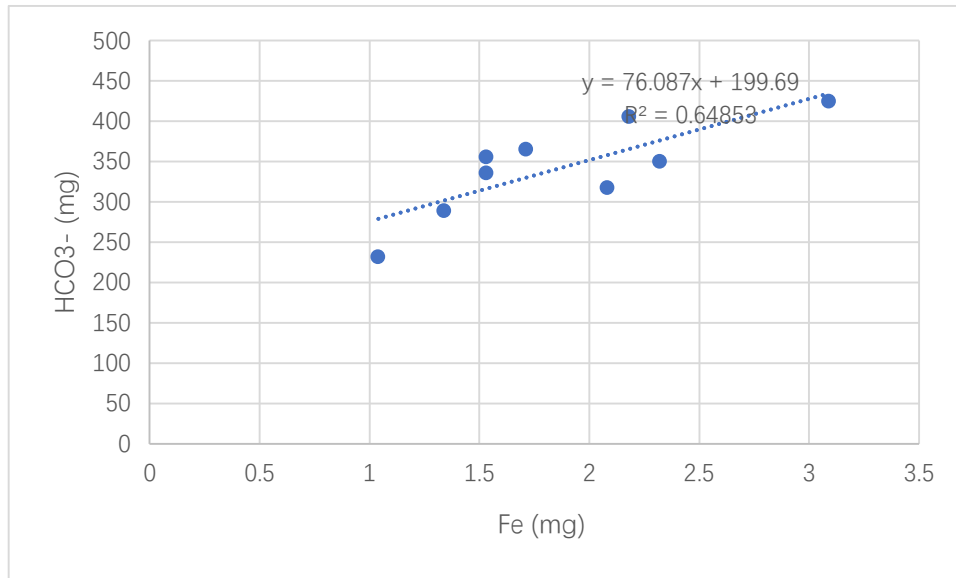## 4.2 The relationship between ions in water.



diagram 4.2.1 relationship of Fe and HCO3-

As can be seen in the diagrams, the $HCO_3$ has strong relationship with Fe (total) value with $R^2$ around 0.7.

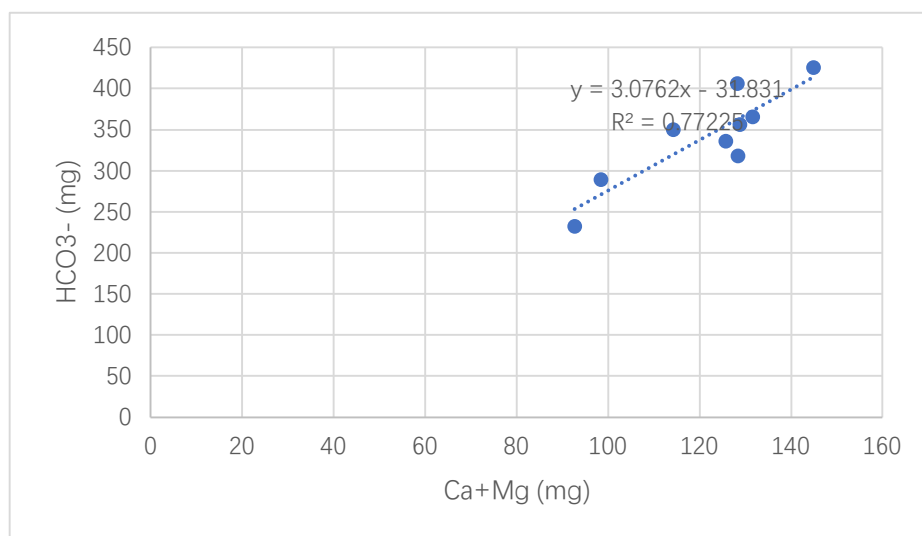Similarly, Ca/Mg is also in proportion to HCO3.



diagram 4.2.2 relationship of Ca/Mg and HCO3-

Therefore, higher concentration of $Ca^{2+}$, Mg and Fe in the GW were maybe the reason for some precipitation, such as Calcite $CaCO_3$, $FeCO_3$.

However, some other relationships between element and element were very week, like that of $SO_4$ and Mg. As can be seen in diagram 4.2.3, the spots were random in the diagram. This may because the concentration of sulfate was quite similar in each well's GW. In this case, the diagram should be discarded [1].
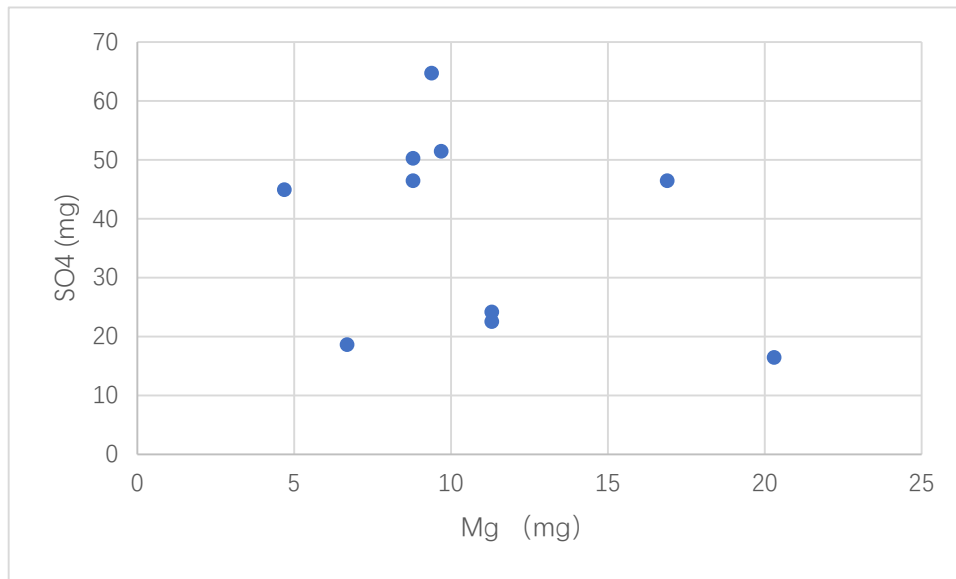


diagram 4.2.3 relationship of Mg and $SO_4$

## 4.3 Determination of sediment

After determining the groups of wells and finding some relationship between some ions or element, Aqion and PhreeqC were used to analyze the sediment of each well.

In Aqion, the raw date of each well was input and then analyzed through adjustment of $Cl^-$ or PH. As the result of adjustment t via $Cl^-$ had less error, the result was therefore recorded in the following table.

Table 4.3.1 Sediment in 10 wells analyzed by Aqion

| Name | Calcite(mM) | Calcit(mg/L) | Siderite(mM) | Fe(OH)3(a) | pH | DIC(mM) |
|---|---|---|---|---|---|---|
| *Brunnen 12* | 0.596 | 61.90 | 0.033 | 0.011 | 7.12 | 8.46 |
| *Brunnen 3.1* | 0.353 | 38.30 | 0.039 | | 7.10 | 7.81 |
| *Brunnen 11* | 0.311 | 33.00 | 0.024 | | 7.13 | 7.46 |
| *Brunnen 7* | 0.158 | 16.80 | 0.012 | | 7.33 | 5.11 |
| *Brunnen 6* | 0.166 | 18.40 | 0.022 | | 7.21 | 5.79 |
| *Brunnen 8* | 0.177 | 19.90 | 0.028 | | 7.21 | 6.36 |
| *Brunnen 4.3* | 0.276 | 28.80 | 0.015 | | 7.16 | 6.67 |
| *Brunnen 9* | 0.086 | 9.21 | 0.008 | | 7.42 | 4.07 |
| *Brunnen 5* | 0.136 | 14.60 | 0.012 | | 7.17 | 6.25 |
| *Brunnen 10* | 0.242 | 25.40 | 0.012 | | 7.17 | 6.52 |

| Name | pCO2(g) | Goethite(mM) | Hematite(mM) | Magnetite(mM) | Pyrite |
|---|---|---|---|---|---|
| *Brunnen 12* | 1.91 | 5.340 | 12.6 | 13.20 | |
| *Brunnen 3.1* | 1.80 | 0.690 | 3.31 | 3.85 | 0.087 |
| *Brunnen 11* | 1.82 | 0.262 | 2.46 | 3.04 | 6.02 |
| *Brunnen 7* | 2.15 | 2.060 | 6.06 | 6.96 | |
| *Brunnen 6* | 1.97 | 0.745 | 3.42 | 4.16 | 2.31 |
| *Brunnen 8* | 1.92 | 0.553 | 3.04 | 3.76 | 3.59 |
| *Brunnen 4.3* | 1.90 | 0.237 | 2.41 | 3.06 | 8.00 |
| *Brunnen 9* | 2.30 | 1.500 | 4.94 | 6.03 | |
| *Brunnen 5* | 1.85 | 1.990 | 5.90 | 6.58 | |
| *Brunnen 10* | 1.90 | 0.497 | 2.92 | 3.58 | 4.47 |

Except the values of PH, DIC, $pCO_2$ which were nearly the same in the 10 well, other sediment was illustrated as follows.
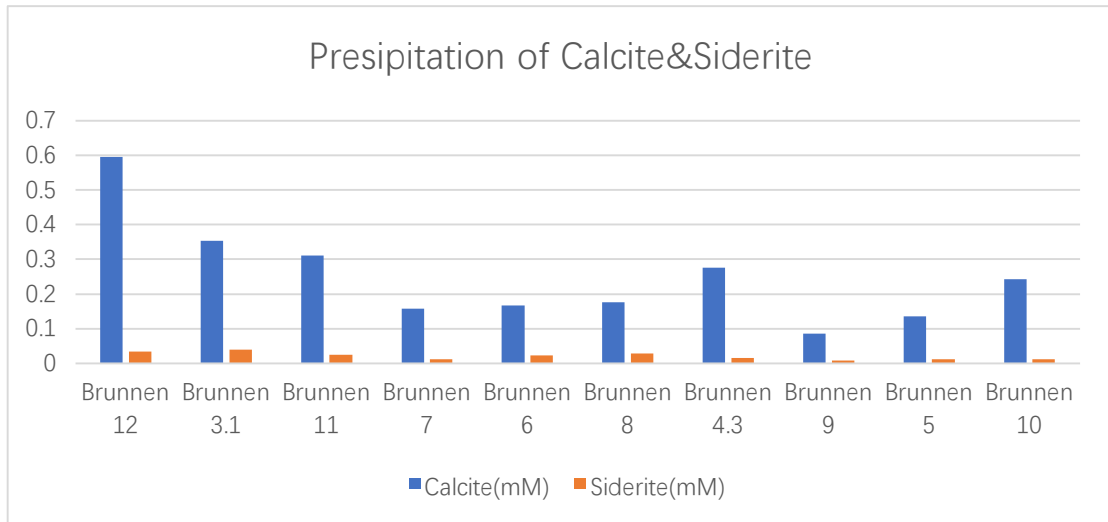
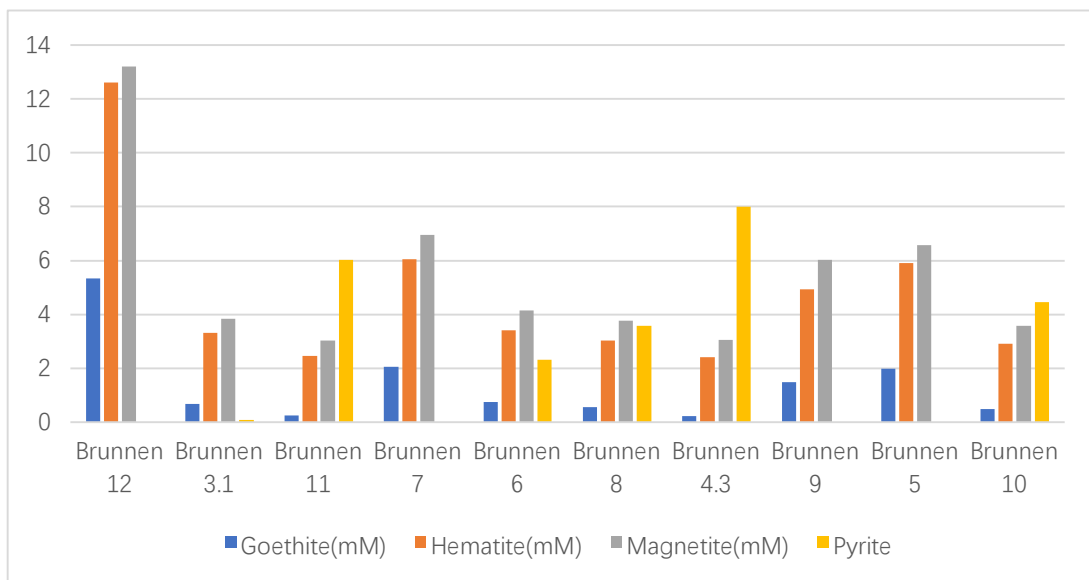Diagram 4.3.1 presipitation of Calcite & Siderite analyzed by Aqion



Diagram 4.3.2 presipitation of Goethite, Hematite, Magnetite, Pyrite analyzed by Aqion

It is very remarkable that all the precipitation in well No.12 were much greater than that in other well. For example, the Calcite in well 12 was 0.6 mM whereas the Calcite in well 4.3, the second greatest, was less than 0.3. Although there is no Pyrite in well 12, the amount of Goethite, Hematite and Magnetite were also far higher than those in other wells.

Beside well 12, well 5,7,9 also precipitated greatly, just following well 12. Conversely, well 9 had least Calcite precipitation.

Table 4.3.2, the result from PhreeqC[1]

| Name | Calcite | Siderite | Goethite | Lepidocrocite | Kalk | Siderit | FeOOH | |
|---|---|---|---|---|---|---|---|---|
| Brunnen 3.1 | 3.04E-01 | 2.03E-01 | 4.12E-01 | 1.14E-01 | C+ | S+ | G | L |
| Brunnen 4.3 | 2.72E-01 | -6.27E-02 | -3.30E-01 | -6.32E-01 | C+ | - | - | - |
| Brunnen 5 | 1.46E-01 | -2.18E-01 | 1.09E+00 | 7.97E-01 | C | - | G++ | L+ |
| Brunnen 6 | 2.07E-01 | -3.39E-02 | 1.29E-01 | -1.57E-01 | C | - | G | - |
| Brunnen 7 | 2.49E-01 | -6.17E-02 | 1.49E+00 | 1.19E+00 | C+ | - | G++ | L++ |
| Brunnen 8 | 2.11E-01 | 8.51E-02 | 5.53E-02 | -2.51E-01 | C | S | G | - |
| Brunnen 9 | 1.85E-01 | -2.17E-01 | 7.07E-01 | 3.97E-01 | C | - | G | L |
| Brunnen 10 | 2.44E-01 | -1.33E-01 | -1.78E-01 | -4.68E-01 | C | - | G | - |
| Brunnen 11 | 2.78E-01 | 6.93E-02 | -1.80E-01 | -4.82E-01 | C+ | S | - | - |
| Brunnen 12 | 5.15E-01 | 4.66E-01 | 2.07E-01 | -1.23E-01 | C++ | S++ | G | - |

Then, PhreeqC (German version) was used in order to check the result from Aqion. After getting the data from Rrofessor Dr.Külls, most of the sediment, as can be seen in Table 4.3.2 [1], corresponded to the result from Aqion. For example, the precipitation of Calcite in well 12 was largest, more than 0.5, which corresponded to the result from Aqion, nearly 0.6.

However, there were some results which were not as same as those in Aqion, including the precipitation of siderite. The reason may be that the amount of total precipitation of siderite in each well was extremely small, and it may be affected by other factors, such as ion strength temperature, greatly.

# 5 Conclusion

## 5.1 The type of well

According to the percentages of ions, the 10 wells can generally be classified as 2 types (2 extremes). Type 1 is well 9 with smallest concentration of hydrogen carbonate and Fe (total) whereas type 2 is well 12 with highest concentration of those ions.

Well 4,3, 5, 6 and 10 are very similar to type 1, as their ion proportions are quite similar to well 9. These 4 types can be recognized as sub-type 1. In contrast, the proportions of ions in well 3.1, 8 ,11 are similar to type 2 and they are recorgnized as sub-type 2. It is also remarkable that well 7 is not similar to either type. Thus, this one is type 3. These three types can be seen clearly in diagrams made by Diagramme, which distinguish each other a lot.

## 5.2 The tendency to precipitate Calcite & Siderite

Calcite was one of the greatest sediment, probably the most, in the well. As those discussed in section 4, well 12, 11, 3.1 were more likely to precipitate this chemical compound. This means that type 2 will precipitate Calcite far more than type 1.

Besides, according to Aqion and PhreeqC, type 2 will also precipitate significantly more Siderite than type 1 does.

## 5.3 The precipitation of Ferrum group

As can be seen in diagram 4.3.2, well 5, 7, 9 3.1 have the greater tendency of Ferrum-group precipitation, like Goethite. This seems that group 1,2,3 all have

tendency to precipitate Ferrum-group; however, there is a parameter directly affect this precipitation —— eH-value.

The reason is that when eH was less than-145, such as well 12 being "-185", the oxygen, nitrate have been fully reduced, and $Fe^{3+}$ will then be reduced$^{2+}$ to $Fe^{2+}$. This means that Ferrum will be less likely to precipitate. Therefore, those eH-value larger than -145 (well 5,7,9,3.1) are more likely to precipitate Ferrum-group, especially well 5, whose eH is -79.

## 5.4 Other precipitation

Other precipitations in these 10 wells are less significant, compared to those above. For example, the amount of Sulfate is extremely low in each well and is too slow to precipitate.

## 5.5 Summary and suggestion

Overall, the type 1 and sub-type 1 is more likely to precipitate, such as Calcite and Siderite. Therefore, if the government want to check the precipitation tendency of a certain well, a diagram from diagramme can help to find the well group and analyze the precipitation. Ferrum-group precipitation has a direct relation with e-H value and is easier to examine since the redox potentiality is rather easier to measure. It is also suggested that the government can compare the precipitation seen from the well and the result from software.

# 6 Reference

[1] Prof. Dr. Christoph Külls, 11. Juli 2019, „Ursachen der Brunnenalterung an Brunnen der Stadtwerke Lübeck Untersuchung der Möglichkeit von chemischer Alterung. "