TECHNISCHE UNIVERSITÄT DRESDEN

Hydrochemistry

Deacidification

Practical Date : Monday, 01.11.2010
Report Delivery : Monday, 22.11.2010

Junianti Roslinda Sihombing

TABLE OF CONTENTS

1. BACKGROUND

1.1 Carbon Dioxide and Carbonic Acid

The most common source of acidity in water is dissolved carbon dioxide. Carbon dioxide enters the water through equilibrium with the atmosphere and biological degradation/photosynthesis involving organic carbon, {CH_2O}. Aqueous carbon dioxide, CO_2 (aq), reacts with water forming carbonic acid, H_2CO_3 (aq).

CO_2 (aq) ⇌ CO_2 (g)

{CH_2O} + O_2(aq) ⇌ CO_2 (aq) + H_2O

CO_2 (aq) + H_2O ⇌ H_2CO_3 (aq)

Carbon Dioxide and Carbonic Acid-Base Equilibrium

Dissolved CO_2 in the form of H_2CO_3 may loose up to two protons through the acid equilibria

H_2CO_3 (aq) ⇌ H^+ (aq) + HCO_3^- (aq)
HCO_3^- (aq) ⇌ H^+ (aq) + CO_3^{2-} (aq)

If nature or chemical agents do not neutralize carbonic acid, it will cause corrosion of both copper and galvanized plumbing systems. Carbon dioxide, together with carbonic acid, is primarily a problem in water containing relatively low concentrations of minerals. In such water there are not sufficient alkaline salts to buffer the effect of the carbonic acid.

Picture 1. The impact of corrosion to the pipe

The methods for removal of carbonic acid are by aeration, filtration by limestone ($CaCO_3$) or half burnt dolomite limestone ($MgO.CaCO_3$) and dosing of Calcium Hydroxide ($Ca(OH)_2$-hydrated lime.

In waters with high levels of dissolved carbon dioxide (carbonic acid) present, aeration for stripping the excess of carbon dioxide reduces the ratio $[H_2CO_3]/[HCO_3^-]$, which results in an increased pH, and therefore lesser aggressiveness/corrosiveness of the water.
By filtration through naturally occuring solid calcium carbonate or limestone, water will react with $CaCO_3$ of the limestone until it reaches the equilibrium pH. The reaction can be summarised as follows:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

The half-burnt filter media, such as half burnt limestone ($Mg.OCaCO_3$) is more frequently used in water treatment systems in industrialised countries, as the amount of filter media used is halved and the necessary contact time is reduced (resulting in smaller volumes).
The reaction is as following:

$$Mg.OCaCO_3 + 3CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

By adding quicklime (CaO) on hydrated lime $Ca(OH)_2$ to water, the water reacts such that the alkalinity and the pH of the water are being raised. The reaction is as follows:

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$$

1.2 Hard Water

Hard water is water that has high mineral content. Hard water minerals primarily consist of calcium (Ca^{2+}), and magnesium (Mg^{2+}) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfates. Calcium usually enters the water as either calcium carbonate ($CaCO_3$), in the form of limestone and chalk, or calcium sulfate ($CaSO_4$), in the form of other mineral deposits. The predominant source of magnesium is dolomite ($CaMg(CO_3)_2$). Hard water is generally not harmful to one's health.

In time the minerals in hard water will settle, forming a hard scale surface which will collect and eventually clog pipes, faucets, toilets, and other water fixtures. This scale frequently forms on the heating elements and heat transfer surfaces in hot water heaters, greatly reducing their efficiency. Laundering and cleaning are made difficult as a result of "soap curd," which is a sticky film formed when soap is used in hard water. Fabrics also wear out and fade more quickly when washed in hard water, and the soap curd can leave cloudy blotches and spots on glassware.

Picture 2. The impact of scale formation in pipe

The following values are used to give an indication about the water hardness:

Table 1. Indication of water hardness

Concentration as CaCO3	Indication
0 to 60 mg/L	Soft water
60 to 120 mg/L	Moderately hard water
120 to 180 mg/L	Hard water
>180 mg/L	Very hard water

There are 2 kinds of hard water, 'temporary' and 'permanent' hard water.

Temporary Hardness

Temporary hardness is caused by a combination of calcium ions and bicarbonate ions in the water. It can be removed by boiling the water or by the addition of lime (calcium hydroxide). Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

The following is the equilibrium reaction when calcium carbonate ($CaCO_3$) is dissolved in water:

$CaCO_3(s) + CO_2(aq) + H_2O \leftrightharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

Permanent Hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence in the water of calcium and magnesium sulfates and/or chlorides which become more soluble as the temperature rises. Despite the name, permanent hardness can be removed using a water softener or ion exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column.

1.3 Langelier Saturation Index (LSI)

The Langelier Saturation Index (sometimes Langelier Stability Index) is a calculated number used to predict the calcium carbonate stability of water. It indicates whether the water will precipitate, dissolve, or be in equilibrium with calcium carbonate. Langelier developed a method for predicting the pH at which water is saturated in calcium carbonate (called pHs). The LSI is expressed as the difference between the actual system pH and the saturation pH.

$$LSI = pH - pHs$$

If the actual pH of the water is below the calculated saturation pH, the LSI is negative and the water has a very limited scaling potential. If the actual pH exceeds pHs, the LSI is positive, and being supersaturated with CaCO3, the water has a tendency to form scale. At increasing positive index values, the scaling potential increases.

In practice, water with an LSI between -0.5 and +0.5 will not display enhanced mineral dissolving or scale forming properties. Water with an LSI below -0.5 tends to exhibit noticeably increased dissolving abilities while water with an LSI above +0.5 tends to exhibit noticeably increased scale forming properties.

Langelier saturation index is defined as:

Table 2. Indication of water hardness

LSI	Scale Potential
Negative, less than zero	No scale potential.
	Water will dissolve $CaCO_3$.
Positive, greater than zero	Scale can form
	CaCO3 precipitation may occur
Close to zero	Borderline scale potential.
	Water quality and temperature changes, or evaporation could change the index.

2. METHODOLOGY

The methodology of this practical is by determining acid and base capacity of the sample water and determining the concentration of Ca^{2+} and Mg^{2+} in the water sample (methodology provided by Lab attached).

3. RESULT

3.1 Experiment Result

For this experiment, the sample water is a tap water combined with carbonated mineral water (Corp. MARGON). A parallel treatment of this carbonate solvent water will be performed in four reactor tubes.

The reactors are filled with several filter materials of the company AKDOLIT GmbH. These materials are used in the large water treatment plants (10.000 m^3/d).

The following parameters of the raw and the treated water should be determined corresponding to the instructions (I/II):

- Temperature and pH value,
- Electrical conductivity κ,
- Total hardness of water, calcium hardness and magnesium hardness,
- Acid capacity $K_{S\,4,3}$ (+m-value) and base capacity $K_{B\,8,2}$ (-p-value),
- LSI value is determined by using LSI calculator.

Table 3. Media filters used in the experiment

Reactor 1	**HYDRO-CALCIT**	**A globe-shaped material made of calcium carbonate ($CaCO_3$)**	
Reactor 2	**HYDRO-KARBONAT**	**A microcrystalline material made of calcium carbonate ($CaCO_3$)**	
Reactor 3	**AKDOLIT-GRAN**	**Porous, dolomitic material ($CaCO_3$,/ MgO),**	
Reactor 4	**MAGNO-DOL**	**A splinter, dolomitic material ($CaCO_3$,/ MgO)**	

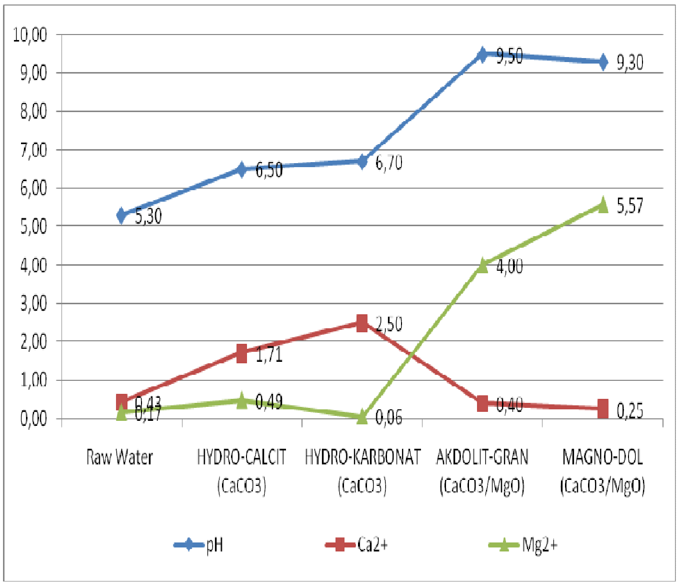
The result of the experiments is showed on the table below :

Table 4. Result of the experiments

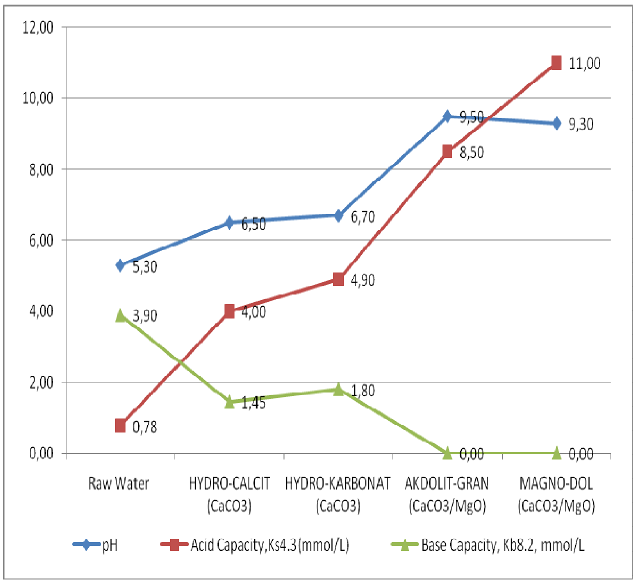
Parameter	Raw Water	HYDRO-CALCIT	HYDRO-CARBONAT	AKDOLIT-GRAN	MAGNO-DOL
pH-value	5.3	6.5	6.7	9.5	9.3
Temperature ϑ ***[°C]***	21.8	22	22.1	22.1	22.3
El. conductivity κ ***[µS/cm]***	164	450	513	625	826
Acid capacity $K_{S\,4,3}$ ***[mmol/L]***	0.775	4	4.9	8.5	11
Base capacity $K_{B\,8,2}$ ***[mmol/L]***	3.9	1.45	1.8	0	0
Calcium-conc. [mmol/L]	0.43	1.71	2.5	0.4	0.25
Magnesium-conc. [mmol/L]	0.17	0.49	0.06	4	5.57
Total hardness [°d H]	3.371	12.36	14.382	24.72	32.7
Saturation index S_I	-3.4	-0.546	-0.604	1.602	1.258

Raw water is the mixture between tap water and carbonated mineral water. The pH-value shows that this water is more acidic. Based on its Calcium and Magnesium concentration, through calculation, it contains 60 mg/L of CaCO3 (**Table 5**) and therefore this raw water is classified as soft water. This kind of water is usually lack of or only has small concentration of Ca^{2+} and Mg^{2+}, which is also shown by the low value of conductivity. The saturation index of the water is -3,4, which indicates that the water has high content of CO^2 and very corrosive.

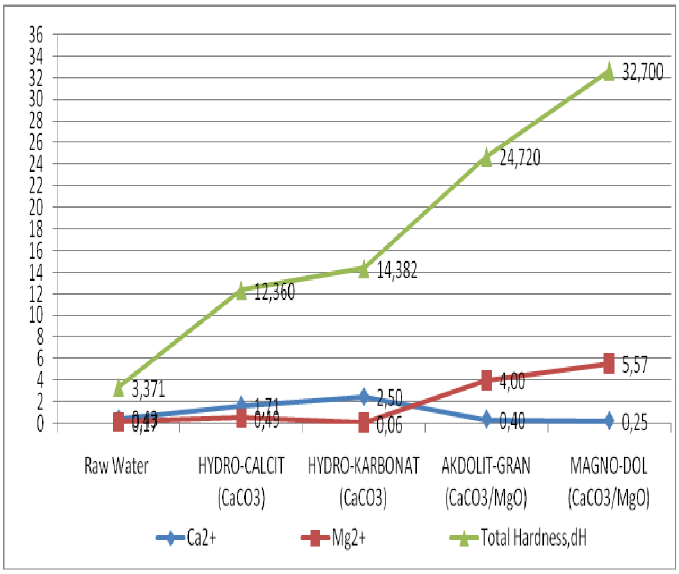
All values of all parameters of all kinds water that are based on the experiments are shown in these graphics:



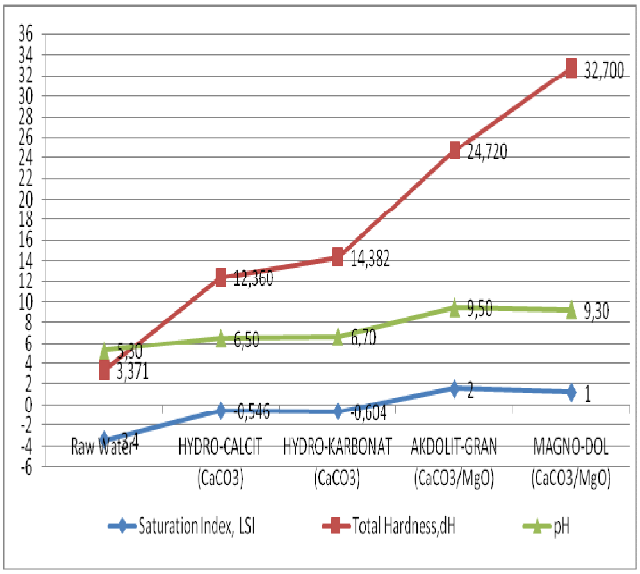
Picture 3. Relationship pH – Ca2+ – Mg2+



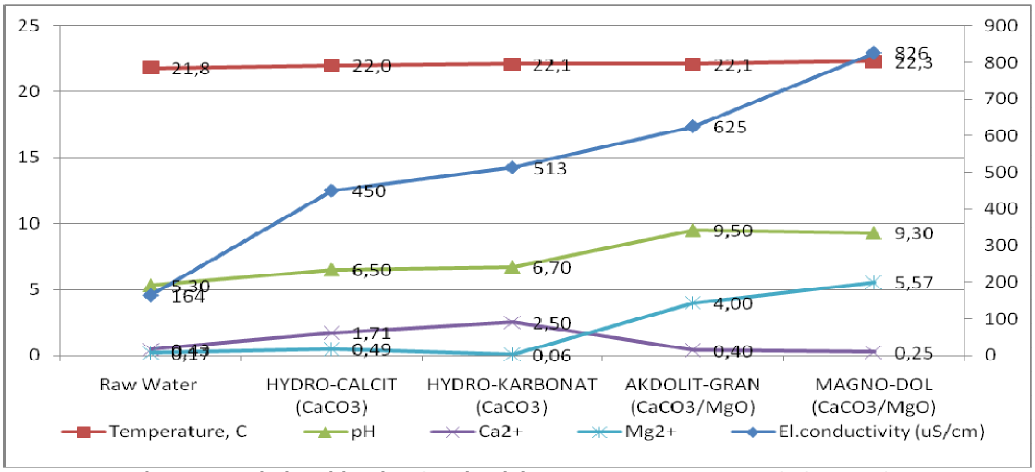
Picture 4. Relationship pH – Acidi Cap. – Base Cap.



Picture 5. Relationship Ca2+ – Mg2+ – Total Hardness



Picture 6. Relationship LSI – Total Hardness – pH



Picture 7. Relationship Elec.Conductivity – Temperature – pH – Ca2+ – Mg2+

• **pH Value**

Water treated with media filters hydro calcit, hydro carbonat, akdolit gran, and magno-dol has the pH-value in the range of 6.5 - 9.5.

The pH values of treated water are still in the range of prevailing drinking water standard in Germany (**attached**). The pH values increase after the water had been treated and the water treated by Akdolit gran and Magno-dol tends to be more basic. This is due to the filters used contain dolomitic material ($CaCO_3$,/ MgO) that is basic.

• **Temperature**

The water temperature of raw water and all treated water do not change significantly. It means that the reactions happening during the filtration do not involve heat/energy transformation (not included either as exothermal or endothermal).

• **Electrical Conductivity**

The electrical conductivity in raw water are 164 ***µS/cm*** and it increases after the water has been filtrated. From all media filters used, the electrical conductivity tends to increase from Hydro-calcit to Hydro-karbonat to Akdolit-gran and then the highest one is Magno-dol.

The electrical conductivity shows the total amount of dissolved ions in the water. The more ions in the water, the more conductive the water resulting in a higher electrical current which is measured electronically. From all values shown in the table, there are more ions dissolved in the water filtrated with Akdolit-gran and Magno-dol compared to all others filtrated water (**Picture 7**).

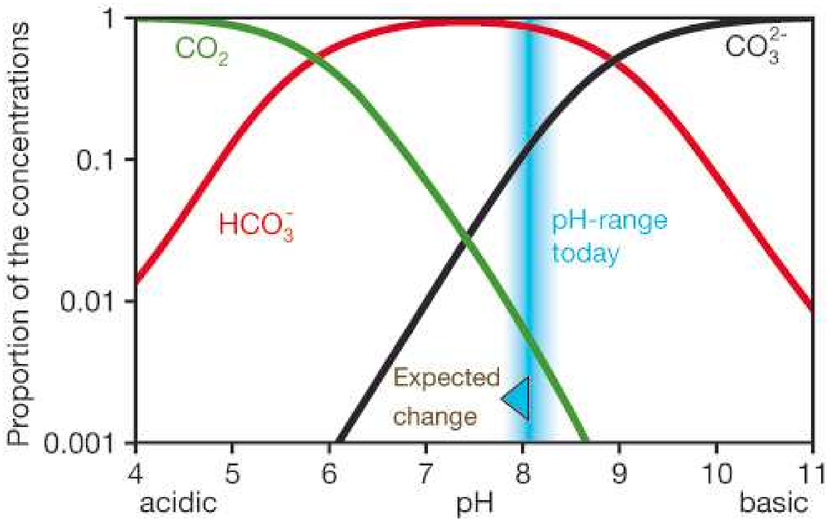
$Mg.OCaCO_3 + 3CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$

The electrical conductivity of the water also depends on the *water temperature*: the higher the temperature, the higher the electrical conductivity would be (**Picture 7**). The electrical conductivity of water increases by 2-3% for an increase of 1 degree Celsius of water temperature. (http://www.smart-fertilizer.com)

Based on The *Drinking Water* Ordinance (TrinkwV 2001), the value of electronical conductivity of water after filtration is still below the standard required, namely : 2500 myS/cm in 20℃ (**attached**).

• **Acid and Base Capacity**

Acid capacity (**$Ks_{4.3}$** in mmol/L) is defined as the capacity of substances contained in water to take up hydronium (H_3O^+) to reach a defined pH value, namely 4.3 . In natural water the hydronium ions are bound mainly by anions of weak acids (mainly carbonate and hydrogen carbonate).



Picture 8. Equilibrium system of carbonic acid

As shown in **Picture 4**, the acid capacity and pH increases after the water has been filtered. From the graphic of equilibrium of system carbonic acid above (**Picture 8**), as the acidity decreases (pH increases), the concentration of the bicarbonate ion tends to decrease, and the carbonate ion increases greatly. After using the filters, the water is more basic and it increases its acid capacity.

Base capacity (**$K_{B8.2}$**, in mmol/L) is defined as the capacity of substances contained in water to take up hydroxide ions (OH^-) to reach a defined value. In natural water this occurs mainly through carbonic acid (sometimes also humic acids) so that the base capacity mainly shows the concentration of dissolved carbondioxide in water.

As shown in **Picture 4**, the base capacity decreases and pH increases after the water has been filtered. From the graphic of equilibrium of system carbonic acid, as the acidity decreases (pH increases), the concentration of the carbondioxide in water decreases greatly. After using the filters, the water is more basic and it decreases its acid capacity. Since the value of pH to be reached is 8.2, therefore the base capacity for water filtrated by Akdolit-gran and Magno-dol is zero (0).

- **Ca^{2+} and Mg^{2+} Concentration and Total Hardness**

The Ca^{2+} concentration in raw water is 0.43 mmol/L and the Mg^{2+} concentration is 0.17 mmol/L. The Ca^{2+} concentration increases but the Mg^{2+} concentration decreases after being filtered by Hydro-Calcit and Hydro-Carbonat. This happens since after filtration there are more Ca^{2+} ions produced in the filtered water.

$CaCO_3(s) + CO_2(aq) + H_2O \leftrightharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

The filtered water by filters Akdolit-gran and Magno-dol has the opposite change. Its Ca^{2+} concentration decreases but the Mg^{2+} concentration increases. This happens since these filters contain Calcium and Magnesium and there are Mg^{2+} ions produced after the water being filtered. The Ca^{2+} concentration decreases since these ions react more and form precipitation. This could be seen by its positive value of LSI (**Picture 6**).

$Mg.OCaCO_3 + 3CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$

Total hardness is defined as the measure of the bicarbonate, calcium, and magnesium ions that present in the water. Total hardness is expressed as mg/l of calcium carbonate ($CaCO_3$), which determines the degree of softness or hardness. From the result of the experiments, the total hardness increases after filtering the water (**Picture 5**). By having the concentration of Ca^{2+} and $Mg^{2+,}$ total hardness is expressed as mg/l of calcium carbonate ($CaCO_3$) as shown in **Table 5**. All water treated by all filters is categorized as very hard water since its content of bicarbonate, calcium, and magnesium >180 mg/L (The indication of water hardness is in **Table 1**). The highest total hardness is in the water filtered with Magno-dol.

Table 5. Total Hardness as mg/l of calcium carbonate ($CaCO_3$)

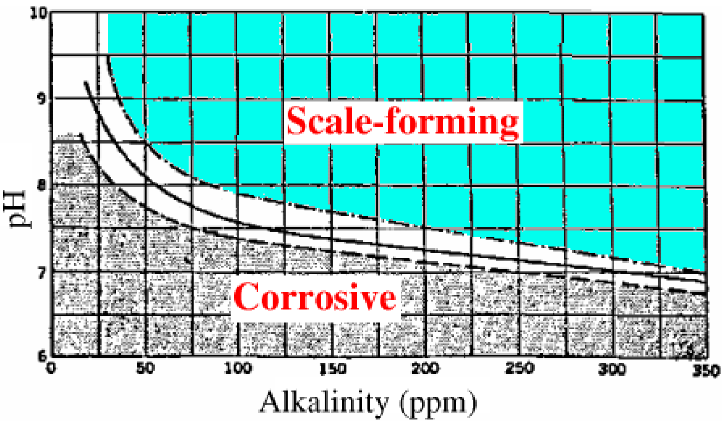
Media Filter	Calcium-conc. [mmol/L]	Magne-sium-conc. [mmol/L]	Total Hardness, German degree	Total Hardness, mg/L of CaCO3	Indication
None/Raw Water	0.43	0.17	3.36	60	Moderately hard water
Hydro-Calcit	1.71	0.49	12.3	220	Very hard water
Hydro-Karbonat	2.5	0.06	14.4	257	Very hard water
Akdolit Gran	0.4	4	24.6	439	Very hard water
Magno-Dol	0.25	5.57	32.5	580	Very hard water

• **Langelier Saturation Index (LSI)**

The LSI value is an indicator of the degree of saturation of water with respect to calcium carbonate. The LSI value of raw water is negative. It means that no scale potential and the water leans toward being corrosive. We can also see this tendency from its pH value that shows that this water is acidic (**Picture 6**).

The water that used media filter Hydro-calcit and Hydro-carbonat has the negative LSI but the values are still in the range -0.5 to +0.5 and this will not display enhanced mineral dissolving or scale forming properties.

The LSI of water that used the filter Akdolit-gran and Magno-dol has the positive value. It is indicative of scale forming . We can also see this from its value of total hardness that water is categorized very hard water . By pH value, the tendency for forming scale could also be seen by using Baylis curve. To know the corrosivity and scale-forming, the pH value and alkalinity are needed.



Picture 9. Baylis curve: The relationship between pH, alkalinity, and water stability

3.2 Advantages and disadvantages

All media can be used as deacidification tools to neutralize acidic water. Hydrocalcit and hydrocarbonat can be used on for water with pH around 5,5 to 7, since they do not give significant increase in pH value. However longer retention on the filter is needed to reach saturation index near 0. In actual application, this kind of media would not be suitable for high pressure filter which has short retention time.

On the other hand, akdolitgran and magnodol, both have high content of Mg^{2+}, and with long retention time, the treated water will have higher degree of total hardness and high saturation index. This condition could work on a raw water with very low pH and low content of Ca^{2+} or Mg^{2+}. For the application, these medias are suitable for high pressure filter which only have short retention time.

3.3 Answer of questions on the last pages of the procedure

- **Total hardness** : the sum of Calcium and magnesium concentration, both expressed as CaCO3, in mg/l.
- **Carbonat hardness (temporary hardness)** : the measure of bicarbonate ($HCO3^-$) and carbonate (CO_3^-) ions in the water.
- **Permanent hardness** : Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence in the water of calcium and magnesium sulfates and/or chlorides which become more soluble as the temperature rises.
- **Acid capacity :** the capacity of substances contained in water to take up hydronium (H_3O^+) to reach a defined pH value .
- **Base capacity** : the capacity of substances contained in water to take up hydroxide ions (OH^-) to reach a defined value.
- **To determine the aggresivity of water,** it is useful to analyze pH, temperature, conductivity, Ca^{2+} concentration and alkalinity (or base capacity as $CaCO_3$).
- **The effect of deacidification materials of calcium carbonate and semiburnt dolomite (equations):**

  $CaCO_3(s) + CO_2(aq) + H_2O \leftrightharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

  $Mg.OCaCO_3 + 3CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$

4. CONCLUSION

1. Hydrocalcit is the filter media that gave the best result to neutralize the raw water with the saturation index of -0,546 and pH fulfills the **TrinkwV 2001** standard. However the high degree of total hardness could cause scale problem.
2. Hydrocarbonate also gave good result in term of saturation index (-0,604 = slightly corrosive). The treated water however still dissolves CaCO3. Longer retention time and addition of CaCO3 would be needed for application.
3. Akdolitgran and Magno-dol both have resulted in high degree of hardness and high saturation index that could result scale forming. The media could be used for filter with short retention time (pressure filter) or water with a very low pH.

5. REFERENCES

Stumm,W; Morgan, J.J: Aquatic Chemistry Chemical Equilibria and Rates in Natural

Hans Hermann Rump: Laboratory Manual for the Examination of Water, Waste Water and Soil

Degremont (2007), Water Treatment Handbook 2, Suez Environment