

Analysis of Corrosion and Anti-corrosion Properties of Solar Heat Transfer Fluids

Abiodun Bamidele Obisesan

Department of Chemistry, University of Jyväskylä, Finland

Email: obisesan.abiodun@yahoo.com

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Abstract

Flat plate collector is commonly used in solar collector because of its uniqueness to operate within low temperature. However, the heat transfer fluid used inside flat plate collector is of great concern lately due to degradation of this fluid over certain period of time. In this work, ethylene glycol water solution was analyzed in the ICP-MS spectrometry and chromatography laboratory. It was established that degradation of ethylene glycol water occurs as function of time due to impurities. This degradation process will ultimately lead to corrosion of solar collector system.

Keywords: Heat transfer fluids, Solar Panel, Ethylene glycol water solution, Heat exchanger

1.0 Introduction

Solar energy and its applications are gaining an increasing role in varieties of ways in the present world economy. The reasons for the increased acceptability of solar energy are that they are safe, sustainable, providing alternatives to tackle increasingly high cost of fossil fuel and environmental problems like pollution and climate change. The application levels of solar energy may include electricity production, use in domestic hot water, industrial heating, space heating and many more. In this view, it is important to develop efficiencies for solar thermal collector that operates within low temperatures ranges. Solar thermal can be used for heating domestic hot water (DHW), outdoor swimming pools (OSP), and ventilation air. Generally, solar thermal applications are either “Active”, implying actively moving solar heat energy to where it is required, or “Passive”, that function in-situ or at source. According to Smyth [1], a simple and efficient approach to utilize solar energy is through direct conversion into thermal energy for various applications such as water heating, desalination, water pumping, air conditioning and cooking. Solar collector is a special kind of heat exchanger that converts radiant energy into heat. In the work of Duffie and Beckman [2], it was elaborated that energy is transferred in solar energy collectors from a distant source of radiant energy to a fluid. The flux of incident radiation is at best, approximately 1100 W/m^2 and its intensity is variable with wavelength from $0.3\mu\text{m}$ to $3\mu\text{m}$. However, the purpose of this work is to examine possible degradation of solar collector materials when in contact with heat transfer fluid.

Figure 1 [3] shows a typical flat-plate collector design. The important parts of typical flat plate solar collectors are “black” solar energy-absorbing surface with means of transferring the absorbed energy to fluid, envelope transparent to solar radiation over the absorber surface that reduces convection and radiation losses to the atmosphere and back insulation to reduce convection losses. In

order to increase the thermal efficiencies, heat has to be transferred efficiently from the absorber to the flowing air, liquid or any other heat transfer medium employed. To improve the efficiency and economics of absorber, solar collector in essence, various authors have proposed modifications to solar absorber: Swarthaw and Ogunade's [4] proposal was to modify the simple absorber flat plate into a solid matrix. Choundhury et al. [5] proposed a corrugated absorber. Gary et al. [6] introduced an absorber plate with film attachment which was susceptible to material problem in resistance to tearing and tear propagation. Parker et al. [7] proposed a V-corrugated absorber plate. Mohamad's [8] suggestion was a porous absorber plate. Kolb et al. [9] proposed a metal matrix absorber plate that improves the thermal performance.

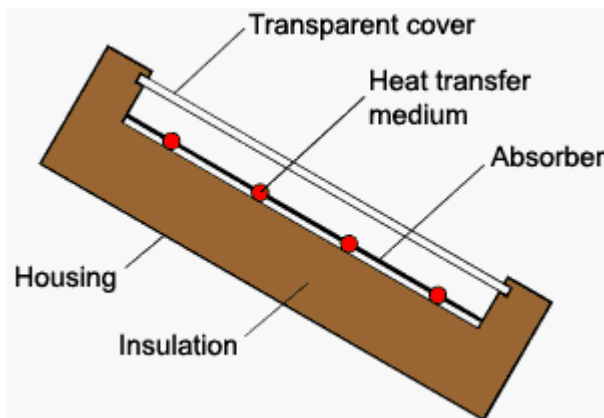


Figure [3]: Typical flat plate collector

2.0 Flat plate solar collectors

Flat-plate solar collectors are perhaps the most common device for solar heat at low temperatures and have been used extensively for both water and heating purposes [10]. They collect energy in form of radiation from the sun; convert it into heat energy, that energy can be used for desired purposes. A typical flat plate collector (Figure 1) consist of absorber, heat transfer medium and insulation material which is usually housed in a casing. The choice of glass as a cover for solar thermal devices is based on the fact that it reflects back almost all the infrared radiation (IR) emitted by the absorber plate.

Aluminum, copper and stainless are a common materials used for manufacturing of solar absorbers. In fact, aluminum and copper are widely used because they exhibit good thermal conductivity. According to Abiola and Otaigbe [11], aluminum alloys are materials choice in use for solar thermal collector system operating on ethylene glycol water solution due to their advantages over other metals. These advantages are light weight, high thermal conductivity, heat and light reflectivity. Aluminum particularly is very resistant to corrosion in neutral or moderately acidic environment and can be used in many cases without any special coating or surface treatment [12]. However, it has been demonstrated [13] that aluminum and its alloys are susceptible to pitting corrosion when they are exposed to an aggressive environment such as chloride media. Also, recent literatures on the use of aluminum and copper suggest that they are weak absorbers of solar radiation. Selective coating is always necessary for the best protection against corrosion. Notwithstanding, copper and aluminum still retain their leading role as base material for absorbers.

2.1 Heat transfer fluid

The term heat transfer fluid refers to fluids that receive and transport energy from cooled objects or heat sources. In solar thermal collectors, especially flat plate collectors, heat absorbed by the solar thermal collector is transmitted or carried to the point where it is released either for space heating or district heating by the heat transfer fluid.

There are different types of heat transfer fluids. Basically water is regarded as the primary heat transfer fluid. Secondary heat transfer fluids contain either water in the mixture or other organic or inorganic compounds in the solution. Typical example of a secondary heat transfer fluid includes ethyl alcohol, calcium chloride etc. Water is an excellent heat transfer fluid [14] as long as the temperature is above 0°C. The problem with water as heat transfer fluid is that, it may freeze during the winter season if it is used in the temperate zones.

Other heat transfer fluids are ethylene glycol/water solution, propylene glycol, ethyl alcohol, calcium chloride and potassium acetate. In flat plate solar collector, ethylene glycol water solution is commonly used due to its non-freezing ability even in cold weather, environmental friendliness and relative low price. Below are the lists of identified properties for good heat transfer fluid [14]:

- a. Sufficient freezing protection
- b. Thermo-physical characteristics i.e. high density, specific heat and thermal conductivity, low viscosity
- c. Corrosion and material compatibility
- d. Environmental aspects especially toxicity, health aspect, biological degradation on ground and water, flammability and other effects on environment

These are important characteristics that have to be considered before the final choice of heat transfer fluids for the solar collector system. Table below highlights thermal capabilities of various solid and liquid materials that can be used as heat transfer medium.

Table 1: Thermal Conductivities of various Solids and Liquids

Materials	Thermal Conductivity, W/(m.K)
Metallic Solid	
Copper	401
Aluminum	237
Non-metallic Solid	
Silicon	148
Alumina (Al ₂ O ₃)	40
Metallic Liquid	
Sodium (644k)	72.3
Non-Metallic Liquids	
Ethylene glycol	0.253

Water	0.145
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2.2 Corrosion in Flat Plate Collectors

Corrosion is the deterioration or destruction of a material through interaction with its environment. It is one of the factors that affect the long-term performance of solar thermal collectors. Corrosion causes a decrease in solar absorptivity and an increase in thermal emissivity, which means an overall loss of performance [13]. Probable source of corrosion in solar thermal collector is the boundary between the heat transfer fluid and the absorber when the fluid is directly in contact with absorber material. Other sources of corrosion can be ageing of heat transfer fluid, unclean surface, joint or other sources. However, focus on this study will be on the boundary between the heat transfer fluid (especially in ethylene glycol/water solution) and the absorber.

Corrosion of metals involves a range of factors. These may be chemical, electrochemical, biological, metallurgical, or mechanical. Nevertheless, the main principle governing corrosion of metals is related to electrochemistry. Corrosion processes in solar thermal collect are therefore of an electrochemical nature which implies that the reactions take place while releasing (oxidation reaction) or taking up (reduction reaction) electron. In order for these types of corrosion to take place, electrons must easily be able to travel in between the places where these reactions take place. For corrosion to take place, it requires that corrosive material is in contact with conductive liquids. Liquids that contain ions in solutions are conductive and this is true for all water based secondary heat transfer fluids including ethylene glycol water solution. Besides, oxygen must be present in order for corrosion to take place. In ethylene glycol water solution, oxygen is present in the solution either through contamination or due to elevated temperature.

2.3 The Pourbaix diagram

A Pourbaix diagram is a thermodynamic map of corrosion, passivity and nobility of a particular metal as a function of system pH and potential [15]. Aluminum is a very reactive metal, but it is also a passive metal. The Pourbaix diagram for aluminum can be used to explain why aluminum corrodes in liquid but is stable in solid concrete. The corrosion of aluminum requires water and the Pourbaix diagram, also known as the potential pH diagram, shows the equilibrium phases for aluminum–water system at different pH potentials. In flat plate solar thermal collectors, where ethylene glycol water solution is used, the presence of water in the solution couple with ethylene glycol being an organic compound can play a vital role in the eventual degradation of aluminum absorber especially when the heat transfer fluid is in contact with the absorber.

In Pourbaix diagram (figure 2), the region of water stability is bounded by the dashed lines labeled (a) and (b). Line (a) is the hydrogen line below which water is no longer stable and decomposes into hydrogen and OH^- (alkalization). The line (b) is the oxygen line above which water decomposes into oxygen and H^+ (acidification). The world's natural environment generally exists within the

regions where water is stable between lines (a) and (b). In acidic conditions (low pH), aluminum will dissolve as Al^{3+} and in alkaline condition (high pH) aluminum will dissolve as AlO_2^- . In neutral pH, from 4 to 8, the hydroxide of aluminum is insoluble and will form a passive film on the aluminum's surface and protect the aluminum [15].

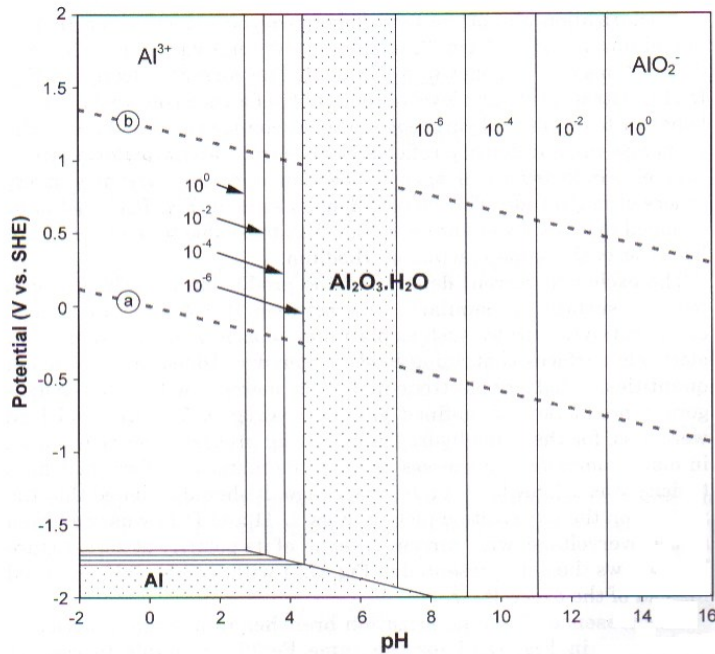
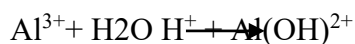


Figure D.10 Equilibrium diagram of Al solid species when soluble species are at a 10^{-6} molar concentration.

2.4 Corrosion Chemistry of Aluminum

Generally, aluminum and its alloys are passive and corrosion resistant in aqueous solution except for pitting corrosion due to some reactive species such as chloride. On the long term, concentration level of ethylene glycol/water that has been spent will play a vital role in the degradation of absorber. The reason for this is that acidic or basic condition will develop along with ageing ethylene glycol water solution in the solar collector. Another important factor that will play significant role in the eventual degradation of flat plate collector is the presence of impurities in the ethylene glycol/water solution. Presence of contaminants in the solution can be due to partial solubility of piping wall of absorber over a long period of time or if the water in the solution is from tap facility. The fact that impurities such as chloride and iron ion are found in the solution is enough to lead to inefficiencies in the system. Such microstructure in the solution may include Fe^{3+} , Cl^- etc. which may lead to formation of electrochemical cells within the system. This in turn may lead to severe attack by pitting in aggressive medium. Corrosion by pitting is a very complex process that can be affected by various factors such as the type of aggressive ion and its concentration, the pH of the media, the temperature or the structural characteristics of the oxide film [14, 16 and 17]. Four stages of pitting corrosion can be distinguished: (a) processes occurring on the passive at the boundary of the passive and the solution; (b) processes occurring within the passive, when no visible microscopic changes occur; (c) formation of so-called metastable pits which initiate and grow for a short period of time below the critical pitting potential and then repassivate (this is an intermediate step in pitting); and (d) stable pit growth, above a certain potential termed the critical pitting potential [17].

Two different types of pit's salt can be identified namely Aluminum chloride (AlCl_3) and aluminum oxy-chlorides $\text{Al}(\text{OH})_2\text{Cl}$ / $\text{Al}(\text{OH})\text{Cl}_2$. Pit's salts are salts that occupy the pits layer within a corrosive metal which has grown considerably over a period of time. Depending upon the kind of salt, different pH of the solution within the pit can be expected [16,17]. This further aggravates the corrosion process. The chemical equation governing this corrosion is as follows:

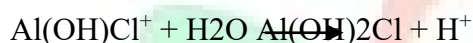


Aluminum hydroxide reacts with chloride:



However, in neutral and alkaline media, the mechanism is related with the formation of protective layer of aluminum hydroxides $\text{Al}(\text{OH})_3$.

In acidic state, solubility of Al^{3+} facilitates the dissolution of aluminum. This further accelerates the chloride attack. The equation governing this process in acidic condition is expressed below:



The essence of aluminum corrosion in ethylene glycol water solution is because protective oxide film on aluminum is not stable in the presence of Cl^- , Cu^{2+} and Fe^{2+} [11]. The Cl^- ion in the solution has the capacity to render the oxide film non-protective, thus activating the metal surface. Particularly in aluminum and its alloy, precipitation occurs with copper ions since aluminum is anodic to copper in the galvanic series with resultant formation of local anodes and cathodes on aluminum surface, resulting in high corrosion rate for aluminum [18].

Therefore, in view of Pourbaix diagram for aluminum and other prevailing factors, it can be asserted theoretically that, ethylene glycol water solution will produce acids in the presence of air (since ethylene glycol/water solution would have been spent – low concentration solutions over time). Concentration level is important in the corrosion of Aluminum. The acids produced have the capacity to attack the protective oxide film of the aluminum due to low level of the pH of the solution. This will result in corrosion of flat plate collector on the long term. Besides, since the flat plate collector will convert light energy into heat energy, there is a high tendency for elevated temperature to be the source of oxygen in the solution. Conditions necessary for corrosion to take place in flat plate solar collector include degradation of ethylene glycol water solution over a long term, pH level drops being below 7 and oxygen level increases at elevated temperature. This is a serious concern for both the end-users and manufacturers if the economic competitiveness is to be maintained.

3.0 Experiment

The purpose of this experimental was to understand composition of ethylene glycol solution after active years of service in a solar collector system. It is important to know whether there will be impurities in the ethylene glycol water solution after it has been in use in solar collector system over a certain period of years. If impurities are present, at what concentration level can they contribute to corrosion of solar collector system? Past works on the corrosion of solar panel had focus on the weight loss that characterized aluminum metal and its alloys in ethylene glycol water solution. Example includes Kontinen's work on thermal stability and moisture resistance of solar absorbers. The work asserted that accelerated ageing test of solar absorber surfaces are used to

estimate the service lifetime of an absorber collector and the work of Olusegun et al. [11] where focus was on the weight loss of aluminium and its alloys.

However, this laboratory work took a divergent view where focus was on the ethylene glycol water solution composition and impurities present.

3.1.0 Semi-quantitative Analysis

Six samples of ethylene glycol water solution were analyzed using semi-quantitative analysis method in the ICP plasma mass spectrometry laboratory. Inductively coupled plasma spectrometry (ICP – MS) is a type of mass spectrometry that is highly sensitive and capable of determination of up to 40 elemental metals and non-metals in a single analysis at a concentration below one part in 10^{12} (parts per trillion). In inductively coupled plasma mass spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulization. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized and excited and/or ionized by the plasma. The radiation is detected and turned into electric signal that are converted into concentration.

Samples analyzed include sample K2_24/07 (contained 42 % concentration of ethylene glycol water solution), Tankki 17/07 (contained 52 % concentration of ethylene glycol), 3.Linja_2/1_12 VAA (concentration of ethylene glycol unknown), and 1.Linja_2/1_12 VAA (concentration of ethylene glycol unknown). Others include sample Std 2 (contained 50 % of ethylene glycol) and Pilotti_L (concentration of ethylene glycol unknown). These samples were collected from different solar thermal systems and all except “Pilotti_L” were several years old. “Old” here refers to the time that the liquid has been used for heat transfer. About 10 ml of each of these samples were filled into the test tubes and diluted with HNO₃ to a factor of 2. Each of the prepared samples was then placed in the ICP plasma equipment for analysis, one after the other. ICP plasma analysis equipment is an efficient system. The analysis period for each of the samples was about 3 minutes per sample and the results were generated automatically. From the generated result, it was observed that sodium concentrations in all of the samples were saturated. However, this was in contrast to what was observed during the analysis which showed that there was a golden flame emitted when each of the samples was under the ICP plasma equipment for analysis. Thus, each of the samples was prepared again as above and diluted with HNO₃ to a factor of 5. It was possible to obtain precise information about sodium concentration level in each of the samples at dilution factor of 5. It took approximately 1 hour to conduct the whole experiment. Extracted information from the ICP plasma analysis is tabulated below.

Table I: Tankki 17/07

Element	Ca	Cu	Fe	Na
Concentration (mg/L)	9.30	0.31	-0.012	1945

Table II: Pilotti_L

Element	Ca	Cu	Fe	Na
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Concentration (mg/L)	14.74	0.26	0.79	2365
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Table III: 3.Linja_2/1_12 VAA

Element	Ca	Cu	Fe	Na
Concentration (mg/L)	15.16	0.56	6.36	1430

Table IV: 1.Linja_2/1_12 VAA

Element	Ca	Cu	Fe	Na
Concentration (mg/L)	6.06	1.59	0.29	1220

Table V: Std 2

Element	Ca	Cu	Fe	Na
Concentration (mg/L)	0.34	0.61	-0.08	2200

- (-) sign indicate that amount present is insignificant

3.1.1 Chromatography Test

ICP plasma technique cannot determine the presence of chloride ion, hence chromatography becomes necessary. The chromatography method followed in this work is known as countercurrent chromatography (CCC) test. This method is a liquid-liquid chromatography test where both the stationary and mobile phases are liquids. The operating principle consists of an open tube coiled around a bobbin. The bobbin is rotated in a double-axis gyrator motion which causes a variable gravity field to act on the column during each rotation. This motion causes the column to see one partitioning step per revolution and components of the sample separate in the column due to their partitioning coefficient between the two immiscible liquid phases used. The type of countercurrent chromatography used during this laboratory work is known as high speed countercurrent chromatography. There is a latest version of this instrument called high performance countercurrent chromatography. As was in the case of ICP plasma analysis, all of the six samples mentioned above were analyzed using countercurrent chromatography test. Samples were prepared according to KOH anions method. About 125 ml of each of these samples were taken, filled into mini flat bottom conical flask where it was diluted with milliQ water. MilliQ water is specially treated water which is almost devoid of impurities. Dilution factor was 10. Approximately 10 ml of each of these samples were filled into test tubes and placed in the analysis chamber of chromatography equipment. Analysis time within the chromatography chamber was about 25 minutes. 3Linja_2/1_12 VAA was the first sample prepared and placed within analysis chamber. While the result was being awaited,

other samples were prepared in a similar way. Prepared samples of K2_24/07, Tankki 17/07, 1.Linja_2/1_12 VAA Std 2 and Pilotti_L were then placed in the analysis chamber after the first analysis had been completed. There were enough compartments within analysis chamber to contain all the samples. Besides, operation of chromatography equipment had been automated. The chromatography equipment was able to analysis each samples sequentially. Spectral analysis results were generated automatically. It took about 3 to 4 hours to complete the whole laboratory work.

3.2 Discussion of Result

3.2.0 Semi-quantitative analysis

Semi-quantitative approach has been employed with great success in inductively coupled plasma by using a single multi- element reference solution that could contain a few selected elements. The concentrations of elements not contained in the reference solution were estimated from previously measured relative response factors with those elements in the solution [19]. In this work, calcium was consistently present in all six samples analyzed. The source of Ca^{2+} is probably from tap water if such water was used to mix ethylene glycol with water. Acceptable level of calcium in the ethylene glycol/water solution is less than 50 ppm. All six samples analyzed contained less than 50 ppm (average value present in all the six samples was 8.51 ppm). However, if the concentration level is above 50 ppm calcium can form scale deposits on the metal surfaces and reduce the thermal performance of the components. Probable reaction for this is:



Copper is compatible with ethylene glycol/water solution. Average concentration level of copper in all the samples analyzed was 0.67 mg/L (0.67ppm). It was not possible to determine at what concentration level copper or its ions will contribute to degradation of ethylene glycol/water solution. However, presence of elemental copper as well as other metals indicates that its salts were present. This result was corroborated by the chromatography test (see appendix diagrams). It was demonstrated by Brown et al. in Ref. [20] that copper (II) salts react with ethylene glycol solution to give copper (II) glycolate, copper (II) formate or copper (II) carbonate depending on the glycolic acid present. Since aluminum is anodic to copper in galvanic series, its presence in an unwanted quantities can result in corrosion of aluminum absorber.

Iron concentrations in the analyzed samples are inconsistent (see Table I-VI above). It was observed during the course of this work that Ca^{2+} , Cu^{2+} , and Fe^{2+} are mutually found in ethylene glycol/water solution exhibiting degradation process. This observation was corroborated by the works of Olusegun et al. [11]. Thus, variations in iron concentrations level as was recorded in the analyzed samples cannot be explained by the ICP plasma analysis and chromatography test alone. Close examination of solar collector that was used and from where the aforementioned samples were collected could provide further explanation for these results.

In addition, there were significant amount of elemental sodium found in the six samples analyzed. Since chloride/water solution is a heat transfer fluid, presence of Na in the samples was not considered as a contributor to eventual degradation of ethylene glycol/water solution on the long term basis.

3.2.1 Chromatography Test

Detailed descriptions about the graphs obtained have been attached. Sample k2_24/07 contained 107.3mg/L (107 ppm), Tankki 17/07 contained 103.87 mg/L (104 ppm), Pilotti_L contained 151.99

(152 ppm), and 3.Linja_2/1_12 VAA contained 99.83 mg/L (152 ppm) components of chloride, sulphide and copper ion. 1Linja_2/1_12 VAA and Std 2 contained 84.8 mg/L (85 ppm) and 102.1 mg/L (102 ppm) same component as above respectively. Spectral analyses obtained from the chromatography test were in consistent with other relevant work especially the work of Brown et al. [20]. This indicative level implies that ethylene glycol/water solution is gradually undergoing degradation.

4.0 Conclusion

Semi-quantitative analysis and chromatography test were carried on the ethylene glycol/water solution in order to determine whether it is undergoing degradation process which in turn could pave way for corrosion process in solar collectors. All the six samples except Pilotti_L analyzed in this work were from solar thermal systems that had been in use for several years and where the heat transfer fluids had not been changed. Pilotti_L was sampled from a solar collector that had been in operation less than a year in Pori. The rest were from the same geographical local but from different solar collector system. It was observed during the course of this work that:

- a. Thermal degradation of ethylene glycol/water solution occurs as a function of time
- b. Eventual degradation of solar collector will occur in part due to degradation of ethylene glycol/water solution.

In view of this, there should be strict adherence by the manufacturer to ensure that tap water facility should not be used to mix ethylene glycol/water solution. Also, possible replacement of ethylene/water solution is recommended every ten to fifteen years. This is because, ethylene glycol water solution would have advance in degradation at ten to fifteen years. Above all, further works still needed to carry out especially on the chromatography test in order to identify the components salts present in ethylene glycol/water solution. Proper identification of salts present will ensure that in a specific target solution.

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