Identifying Chloride Content For Corrosion Under Insulation By Analytical Technique

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Abstract: Corrosion can be defined as the destruction or deterioration of materials due to the electrochemical reaction with the environment. The factors that affect corrosion attacks include temperature, oxygen, pH and chloride. It is possible to describe proportion of chloride dissolved in solution contribute to salinity value. The purpose of this analysis is to measure amount of chloride content in water ingress absorbed in the insulation material. The temperature used in this research is 27 ºC and the salinity ranges from 1 %, 2 %, 3 %, 3.5 % and 4 %. Due to strong similarities between the salts and lack of motivation to distinguish between all of them, spectral differences of concentration between an aqueous solution of NaCl have received minimal attention in previous research. The results show that correlating spectral measurements and the concentration of NaCl in liquid water can be applied up to the saturation point of salts and that solution of these salts of uncertain concentrations can be differentiated. Spectral data were obtained for NaCl samples and their concentrations were measured with an average error of 0.9 %. From this analysis, it is concluded that the corrosion rate can be caused by environmental conditions such as salinity concentration.

Keywords: Absorbance, NaCl, Salinity, Spectroscopy, Water

1. Introduction

Corrosion Under Insulation (CUI) is a serious form of localized corrosion that affects insulated engineering devices usually used in oil and gas production. The undetected or unmitigated production of CUI in oil and gas equipment may have implications such as metal perforation of steel piping and gas leakage in liquid natural gas (LNG) plants [1]. Therefore, the expense of detecting, tracking and regulating CUI accounts for a significant fraction of the maintenance expenditure of the oil and gas producers. Therefore, the development of a technically feasible approach for the protection of insulated steel equipment is of great interest to the industrial community [2].

Latest CUI mitigation studies have focused on how moisture can be separated from insulation and insulated equipment. To ensure effective field implementation of a best practice insulation specification, caution must be taken in creating and designing all components of the specification. Deficiencies in some of the components can and do cause the insulation system to fail prematurely. Next, the choice of

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insulation materials and their application is of vital importance for the design of the insulation system [3].

Corrosion under insulation (CUI) is recognized as a major corrosion problem, which costs the oil & gas, petrochemical and chemical industries millions of dollars a year in inspection, repair and maintenance costs. The covered of the insulation material over the pipe that encourage the build up of moisture and not allowing the evaporation process occur. Hence, it would accelerate the corrosion rate.CUI can occur under any type of insulation depending on the type of metal which is insulated or other related factors. For example, rockwool, fiberglass, or other traditional types of insulation promote corrosion, and also act as a carrier and spread the corrosion because of water may get trapped inside insulation. Further, absence or poor condition of coating the insulation and elevated temperature may promote the CUI. Thermal insulation is necessary component of the pipeline system and is designed to save energy and control process temperatures.

2. Materials and Methods

2.1 Materials

Rockwool is an extremely popular growing medium in the hydroponics community. It's composed of two natural ingredients, basalt rock and chalk, that are heated to 3000°F and 'spun' and cooled, transforming it into a material that is perfect for a plant's root zone. Rockwool is great a balancing moisture and oxygen, which provides a perfect middle ground to prevent over-watering or under-watering. It's fibers don't restrict the accessibility of nutrients for the plant as it provides an ideal medium for nutrient uptake.

Preparation of sodium chloride (NaCl) solution is an important matter in conducting this experiment. There are five different concentrations that is used for this experiment which are 1%, 2%, 3%, 3.5%, 4% according to the standard ASTM C871. The following procedures is the example of preparation for 3% concentration of sodium chloride (NaCl).

Procedure in preparing 3% concentration of NaCl, started with measure 15g of sodium chloride (NaCl) by using digital weighing machine. The weighted poured in 500ml of distilled water in a beaker to get 3% of NaCl salinity. Followed by stirred it using hotplate stirrer to make sure it fully dissolved as shown in Figure 3.6. The solution was poured and keep in a bottle. The same steps were repeated for other solution of 1%, 2%, 3.5% and 4% concentration of NaCl. Then, immerse the rockwool to each solution for 15 minutes. Finally, dry the rockwool using the oven for 45 minutes and the samples are ready to run FTIR test.

2.2 Methods

The method by which the interaction between radiation and matter is studied as a function of wavelength is infrared spectroscopy. IR spectroscopy in modern laboratories has quickly become a common technique. Analytical techniques for preparatory and analytical chemists are the core applications of IR spectroscopy.

The IR region of spectroscopists is split into the near, mid and far infrared in comparison to the visible light spectrum. The boundaries between these regions are not clearly defined and, thus, the various publications differ [4]. The Fourier Transform Infrared (FTIR) machine brand that used in this project was Perkin Elmer model with spectrum 100 and the Spectrum Express software was used to get the data. Specimens were checked using the Fourier Transform Infrared (FTIR) machine seen in Figure 1 by putting on the machine 12 sample forms one by one. And, after the scanning process is completed, the type of factor that appears in the material of each sample can be determined.
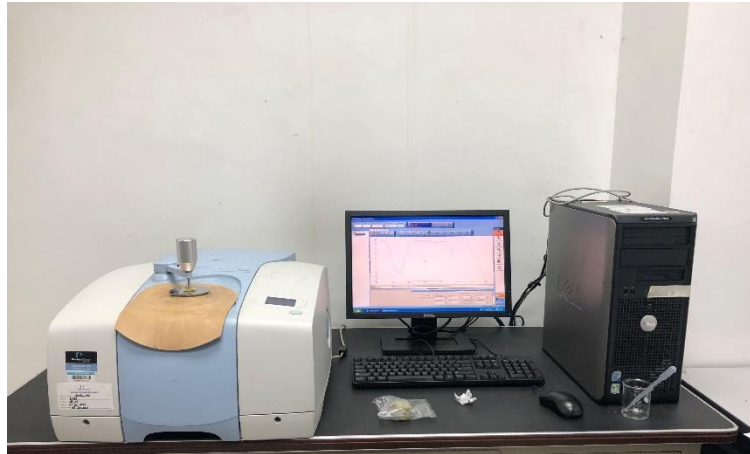
Figure 1: Fourier Transform Infrared (FTIR) machine

The method mentioned here is attenuated total reflection (ATR) for a single reflection. Using a typical FTIR spectrometer, the infrared beam passes through an attenuated total reflection (ATR) placed within the sample compartment instead of being transmitted through the cell and sample. The beam comes from the interferometer and passes through the mirror and lens system of the attenuated total reflection (ATR) device. It moves to the back of the crystal via a non-absorbing crystal to undergo internal reflection. This is the interface between the crystal and the probe at the same time. The internal reflection, unlike the name suggests, is not complete after all.

It attenuates the reflection. A small part of the wave, the evanescent wave and penetrates the interface and interacts with the probe. For any wavelength, this evanescent electrical field can be observed. The IR beam lost a bit of the energy that the probe absorbed and now contains structural data. The detector ultimately picks up the signal.

3. Results and Discussion

3.1 Investigation on chloride salts

To obtain chemical structures of rockwool, Fourier Transform Infrared (FTIR) spectroscopy was recorded with FTIR machine followed ASTM G187-07 standard, which have attenuated total reflection (ATR) accessory. The measurements were applied between $4100cm^{-1}$ – $600cm^{-1}$ wavelength. This range where refer to the mid-infrared which is to study fundamental vibrations such as the OH stretching vibrations [5]. Different concentration of sodium chloride (NaCl) was found to have very close absorption spectra, consistent with previous studies. However, a few regions were observed where the form and intensity varied. Absorbance results from 2.5 to 25 µm were gathered and showed strong alignment with previous ultraviolet and visible studies. Figure 2 shows a typical spectrum of rockwool with 0% concentration of NaCl.

The large positive peak which generally appears around $876.14cm^{-1}$ - $875.11cm^{-1}$ is attributed to carbon-hydrogen molecules. The spectral changes induced by the two samples are comparable, but there are differences in spectral shape and correlation between concentration and absorption change in this region. Figures 3 shows a spectrum of 1% concentration of NaCl. The positive peak value, which normally occurs around $3368.99cm^{-1}$ – $3368.53cm^{-1}$, is due to anions bound through hydrogen to water molecules that directly affect the OH bond. Although the intensity value is about 0.15A-0.24A, the different intensity of the peak of the network was associated with the dissolved ions' various structure making or breaking behaviour. The absorption bands also situated between $1636.32cm^{-1}$ – $1635.46cm^{-1}$. This peak illustrates the C=O conjugated stretching vibrations. Those peaks are dependent on concentration of sodium chloride (NaCl) and corresponds to the second overtone of the symmetric and asymmetric OH-stretching bands [6].
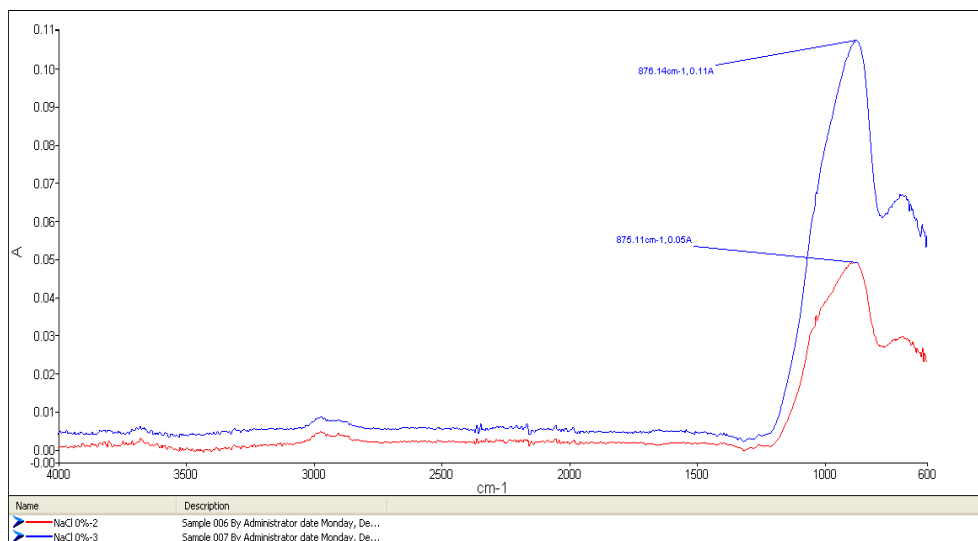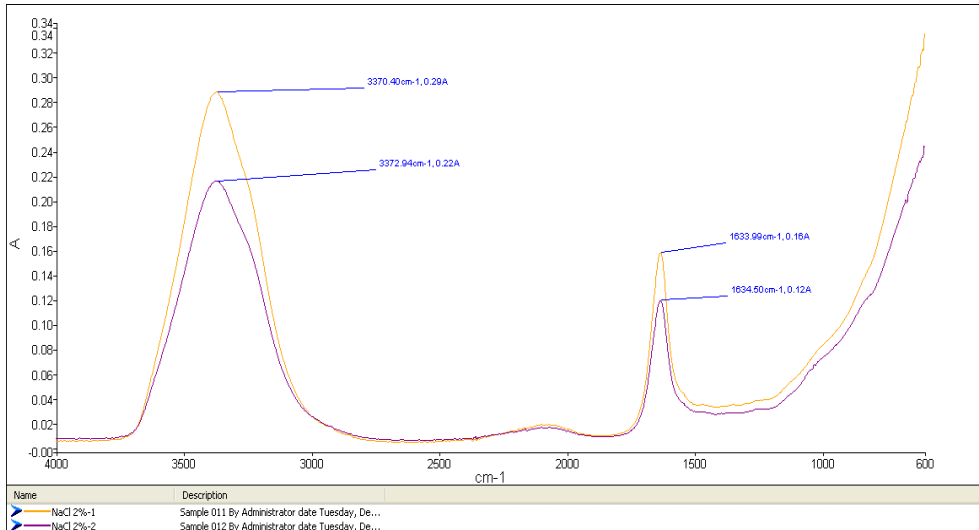
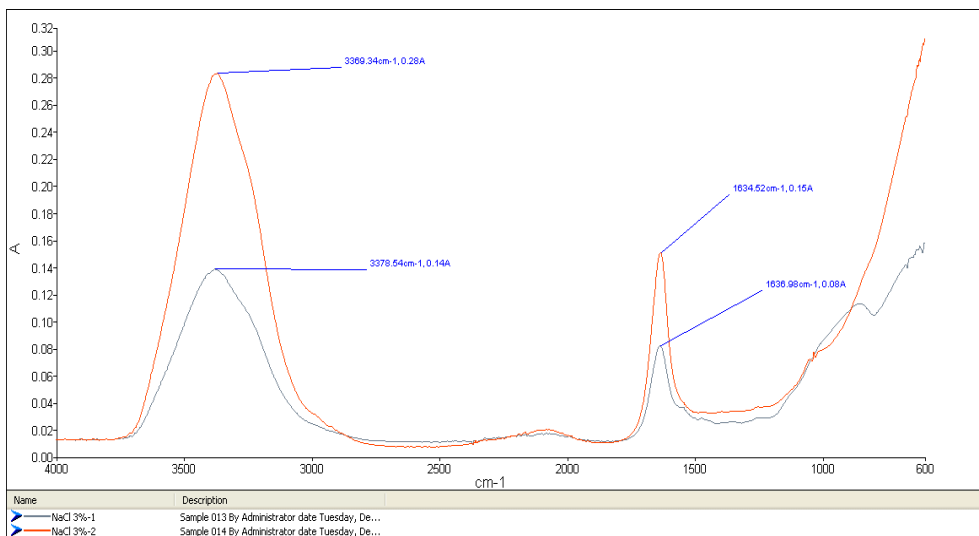**Figure 2: FTIR spectrum of 0% Concentration of NaCl.**
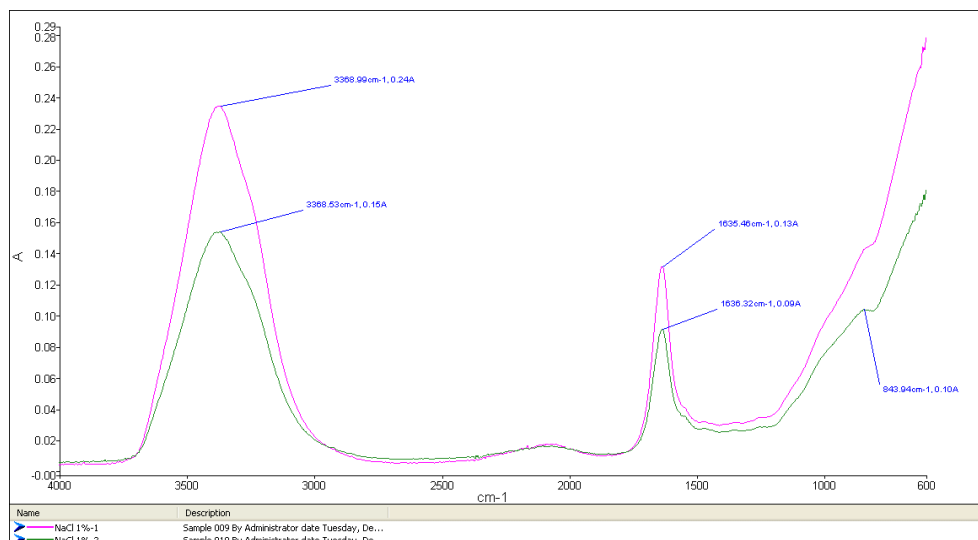
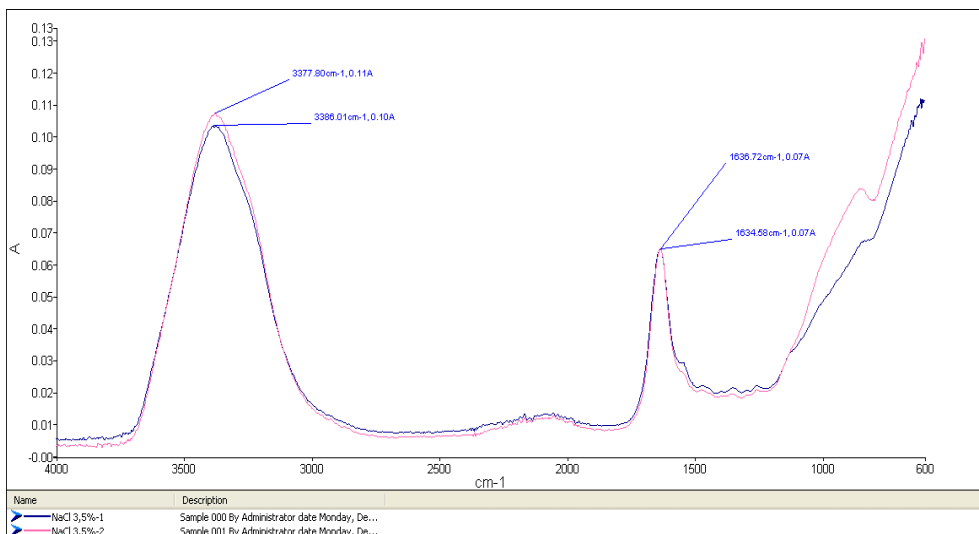**Figure 3: FTIR spectrum of 1% Concentration of NaCl.**

Figures 4 shows that the large network peak is around 3372.94cm^{-1} – 3370.40cm^{-1} which means it is also attributed to anions bonded to water molecules via the hydrogen directly influencing the OH bond. The second peak which is around 1634.50cm^{-1} – 1633.99cm^{-1} which give the same result with 1% concentration of NaCl. This attributed the C=O conjugated stretching vibrations. The same goes for the graph in Figures 5 with 3% of concentrations. It gives the peak value around 3378.54cm^{-1} – 3369.34cm^{-1} and for the second peak which give the value around 1636.98cm^{-1} – 1634.52cm^{-1}. For the 3.5% concentration of NaCl, the large value for both graphs is 3386.01cm^{-1} – 3377.80cm^{-1}. It shows that the chemical bonding appears is intermolecular hydrogen bonds. On the other hand, the second peak gives the value around 1636.72cm^{-1} – 1634.58cm^{-1}. This value represents the C=O conjugated stretching vibrations. Infrared spectra of many carboxylic acid especially in acyl chlorides a lower intensity shoulder or peak near 1700cm^{-1} is due to an overtone interaction.

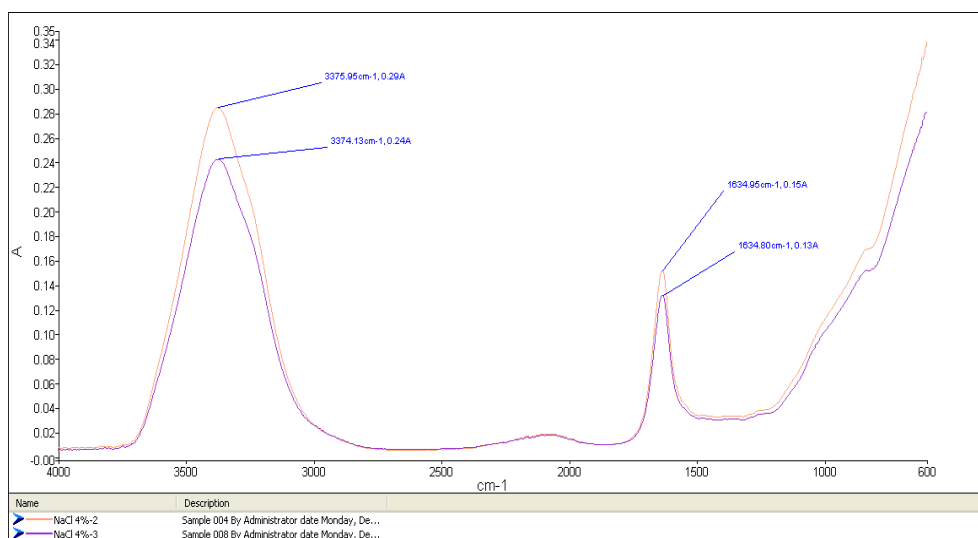**Figure 4: FTIR spectrum of 2% Concentration of NaCl.**

Figure 5: FTIR spectrum of 3% Concentration of NaCl.

Figure 6: FTIR spectrum of 3.5% Concentration of NaCl.

Figure 7 shows a spectrum for 4% concentration of NaCl. It gives the peak value around $3375.95cm^{-1}$ – $3374.13cm^{-1}$ which contains the same chemical bonding since we are using the same salt solution but only with a different concentration. Same goes with the second peak which gives the value around $1634.95cm^{-1}$ – $1634.80cm^{-1}$. This value also attributes the C=O conjugated stretching vibrations.

Figure 7: FTIR spectrum of 4% Concentration of NaCl.

3.2 Anion dependency

The ions are routinely modified to observe different features of the OH stretch bond depending on the ion. The cation is kept constant for anionic specificities when altering the anion. The concentration is exchanged to learn more about cationic behaviour. Although the influence of the cation is very minimal, a strong anionic effect on the strength and location of the OH stretch band is prominent. The cationic dependence on the largely positive and the large negative contribution is restricted to very slight changes in the positioning of the band.

Table 1: Average Intensity and Wavelength for First Peak of All the Concentration of NaCl.

Concentration of NaCl (%)	Intensity (A)	Wavelength (cm^{-1})
1	0.20	3368.76
2	0.26	3371.67
3	0.21	3373.94
3.5	0.11	3381.91
4	0.27	3375.04

**Table 2: Average Intensity and Wavelength for Second Peak of All the Concentration of NaCl.**

Concentration of NaCl (%)	Intensity (A)	Wavelength (cm^{-1})
1	0.11	1635.89
2	0.14	1634.25
3	0.12	1635.75

3.5	0.07	1635.65
4	0.14	1634.88

For all concentrations, estimating the average change shows very similar results. In that specific area, the wide peak can be attributed to the anion influencing the OH stretch band. Besides, for the second peak attributes the C=O conjugated stretching vibrations bands. This understanding is confirmed by the results of this research. A profound anionic dependent behaviour is shown by the broad peak. The peak of the network is less anion-influenced. One does also not expect the anion bound to the OH group by hydrogen to decrease the strength of this particular OH bond. A profound anionic dependent activity is shown by a large positive peak. The peak of the network is less anion-influenced. One does also not expect the anion bound to the OH group by hydrogen to decrease the strength of this particular OH bond. Just the same, due to the shift of the transition dipole moment, a heavy binding anion will increase the strength of the OH bond.

3.3 Cation dependency

Cation's effect on the location of the band is very weak. For Na^+, variations in peak heights can be observed. Na^+, which is the cation, may also affect the anionic peak. The same OH group interacts with one anion and one cation, the anion directly with hydrogen, the cation through oxygen. Because of its high charge density and further-reaching influence, cooperative effects contribute to the cation promoting the anion effect and causing a major change from the anionic peak to lower wavenumber. Charge density for Cl^- is higher, so the positive anionic peak goes down to lower wavenumbers and the two contributions fuse, allowing NaCl to vanish from the negative dip. Figure 8 shows the exact proportion of the sodium chloride solution. Each material for industrial insulation reacts to water and different humidity. The typical testing of insulation materials is for absorption of water vapour, water wicking, submersion of water before delivery from the liquid, or entrained water in the material fabrication workshop. For this research, water vapour absorption was analysed based on ASTM C1104 standard.
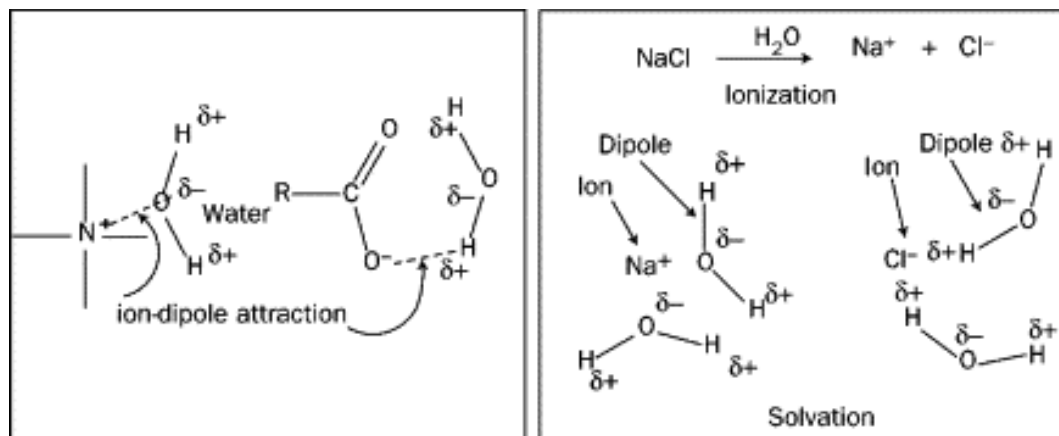
Figure 8: Ions in solution in exact proportion

3.4 Sodium and hydrophobicity

In general, when water is repelled from a material or a molecule, hydrophobicity occurs. It seems odd to talk about water being repelled from a charged ion, but the concept behind this phenomenon can be observed also for charged ions. The number of free OH groups is almost unchanged and the hydrogen-bonded network almost remains in this position, it is less probable that precipitation will occur. Hydrophobic solutes are also known to cause water to tangentially organize itself around such a

particle. A polar or hydrophobic solute are often considered to suggest that water can arrange itself in a tangential way around. This means that similar to what can be seen for clathrate hydrates, a cage-like structure is built around it [7]. This retains the maximum number of hydrogen bonds, which in turn will mean the existence of fewer quasi-free OH groups.

No proof of strong hydrogen bonds between the nearest water molecule and the anion could be found for NaCl in solution, so Cl⁻ could be considered hydrophobic. This finding supports the sophisticated based on the article by Raman on the same topic [8]. On the other hand, the strong decrease in the infinite bonded hydrogen network, which must occur naturally, is caused by the greater existence of local disorder-causing solutes. Water and moisture are referred to differently by any industrial insulation material. Insulation products are usually tested before shipping from the production plant for water vapour sorption, water wicking, submersion of water or entrained water in the insulation. The easiest way to deal with CUI is to prevent water from accessing the isolation device in the first place. If water makes its way past the jacket, the use of water repellent additives for insulation fabrics stops water from penetrating the isolation device.

4. Conclusion

In conclusion, the results obtained in this study clearly show that attenuated total reflection ATR-FTIR reflection spectroscopy can be effectively extended to the qualitative and quantitative examination of rockwool under various concentrations of sodium chloride. The method is swift and non-destructive, relatively safe to use, and most notably does not require sample pretreatment, offering great benefits as it was not possible to use regular IR transmission due to issues of phase transformation. Finally, it should also be noted that while this analysis was undertaken solely to demonstrate the viability of the ATR-FTIR technique for the characterization of rockwool in sodium chloride (NaCl) solution, the data provided here indicate that in situations where batch polymorphic purity, consolidated consistency assequent consistency, the technique can theoretically provide highly tailored, fast and reliable information.

Sodium chloride (NaCl) alkali halides are also used due to their good infrared propagation. However, this substance is highly porous and not resistant to moisture. Consequently, such aperture plates cannot be used for solutions containing water or low-grade alcohol. The calculated wavenumber spectrum often needs to be weighed when selecting the aperture plates. For example, because NaCl offers transmission only down to 650cm^{-1} on the low-wavenumber side, it cannot be used to achieve a bandwidth over the 600cm^{-1} to 400cm^{-1} range. From this analysis, it can be concluded that chloride content can be identified by analytical techniques to solve CUI. From this, we can measure the environment corrosion rate due to salinity concentration.

Acknowledgement

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